Evolution of Modern Pipeline Steels

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- A materials scientist has to consider four ‘intertwined’ concepts, which are schematically shown as the ‘Materials Tetrahedron’.
- When a certain performance is expected from a component (and hence the material constituting the same), the ‘expectation’ is put forth as a set of properties.
- The material is synthesized and further made into a component by a set of processing methods (casting, forming, welding, powder metallurgy etc.).
- The structure (at various length scales) is determined by this processing.
- The structure in turn determines the properties, which will dictate the performance of the component. The Materials Tetrahedron The Materials Tetrahedron
- Hence each of these aspects is dependent on the others.
- The broad goal of Metallurgy Metallurgy & Materials Materials Engineering is to understand understand and ‘Engineer’ ‘Engineer’ this Tetrahedron

What determines the properties of materials?

- The following factors put together determines the properties of a material:
- Composition Phases & Their Distribution Defect Structure Residual Stress Hence, one has to traverse across lengthscales and look at various aspects to understand the properties of materials
- The following factors put together determines the properties of a material: Composition Phases present and their distribution Defect Structure (in the phases and between the phases) Residual stress (can have multiple origins and one may have to travel across lengthscales)
- These factors do NOT act independent of one another (there is an interdependency)

Hence, one has to traverse across lengthscales and look at various aspects to understand the properties of materials

- In order to understand the structure of materials and its correlation to property, we have to start form the basic element of matter – The Atom
- As we know, common to all materials is that they are composed of atoms.
- The properties (whether mechanical, electrical, chemical etc) of all solid materials are dependent upon the relative positions of the atoms in the solid (in other words the atomic structure of the material) and their mutual interaction i.e. the nature of the bonding (whether e.g. covalent, ionic, metallic, van der Waals).
- There are examples of where the atom-atom interactions is strongly reflected in the atomic structure. An example is diamond. Here the carbon-carbon interactions lead to a very directional covalent bond called a sp3 bond which has tetrahedral symmetry symmetry –
- Of course carbon can also take the form of graphite. Here the carbon atoms are arranged in a rather different structure and graphite has very different properties to diamond!

- In other solid systems (for example many of the metallic elements) the atomic structure is dictated by how well we can ‘pack’ the atoms into 3D space – ‘packing efficiency’ – this leads to dense close-packed structures as we will also discuss in crystal structure chapter.
- So it is vital that to understand the properties of material, and to improve those properties for example by adding or removing atoms, we need to know the Role of atomic structure in materials properties for example by adding or removing atoms, we need to know the material’s atomic structure.

Atomic Interaction

- When two neutral atoms are brought close to each other, they experience attractive and or repulsive force.
- Attractive force is due to electrostatic attraction between electrons of one atom and the nucleus of the other. Repulsive force arises due to repulsion between electrons and nuclei of the atoms.
- The net force, F N (Fig) acting on the atoms is the summation of attractive and repulsive forces.
- The distance, at which the attraction and repulsion forces are equal and the net force is zero, is the equilibrium interatomic distance, r o .
- The atoms have lowest energy at this position. Attraction is predominant above r o and repulsion is dominant below ro.

Atomic Bonding

- The mechanisms of bonding between the atoms are based on the foregoing discussion on electrostatic inter- atomic interaction.
- The types of bond and bond strength are determined by the electronic structures of the atoms involved.
- The valence electrons take part in bonding. The atoms involved acquire, loose or share valence electrons to achieve the lowest energy or stable configuration of noble gases.
- Atomic bonding can be broadly classified as i) primary bonding ii) secondary bonding

Type of atomic Bonds

- Primary Bonds :
  - > Ionic,
  - > Covalent,
  - > Metallic
- Secondary Bonds:
  - > Vanderwaals,
  - > Hydrogen

Majority of the engineering materials consist of one of these bonds. Many properties of the materials depend on the specific kind of bond and the bond energy

- Properties of a material are determined by two important characteristics: Atomic structure Electromagnetic structure – the bonding character (Bonding in some sense is the simplified description of valence electron density distributions)
- There are microstructure ‘sensitive’ properties (often called structure sensitive properties) and microstructure insensitive properties (note the word is sensitive and not dependent).
- Microstructure ‘sensitive’ properties → Yield stress, hardness, Magnetic Summary
- Microstructure ‘sensitive’ properties → Yield stress, hardness, Magnetic coercivity… Microstructure insensitive properties → Density, Elastic modulus…
- Hence, one has to keep in focus: Atomic structure Electromagnetic structure/Bonding Microstructure to understand the properties.

Ionic Bond

- Ionic bonds are generally found in compounds composed of metal and non-metal and arise out of electrostatic attraction between oppositely charged atoms (ions).
- Number of electron in outer shell is 1 in Na and 7 in Cl . Therefore, Na will tend to reject one electron to get stable configuration of Ne and Cl will accept one electron to obtain Ar configuration.
- The columbic attraction between Na^+ and Cl^- ions thus formedwill make an ionic bond to produce NaCl.

Covalent Bond

- In this type of bonding, atoms share their valence electrons to get a stable configuration.
- Methane (CH4): Four hydrogen atoms share their valence electrons with one carbon atom and the carbon atom in turn shares one valence electron with each of the four hydrogen atoms. In the process both H and C atoms get stable configuration and form a covalent bond.
- Covalent bonds are formed between atoms of similar electro negativity.
- C atoms in diamond are covalently bonded to each other. Si also has valency of four and forms SiC through covalent bonding with C atoms.

Metallic Bond

- In metals the valence electrons are not really bound to one particular atom, instead they form a sea or cloud of valence electrons which are shared by all the atoms. The remaining electrons and the nuclei form what is called the ion core which is positively charged. The metallic bond arises out of the columbic attraction between these two oppositely charged species – the electron cloud and the ion cores. Electron cloud distribution in various kinds of bon

Concept of Thermal Expansion

- The length of a bond is defined as the center-to-center distance of the bonding atoms. Strong bonds pull the bonding atoms closer together and so have smaller bond lengths as compared to weak bonds.
- Primary bonds have lengths in the range 1-2 Å (0.1-0.2 nm). Secondary bond lengths are larger, in the range 2-5Å (0.2-0.5 nm) Some ambiguity in this definition arises if the element in question, exhibits different crystal forms.
- For example, the diameter of the iron atom is 2.48 Å when it is surrounded by eight neighbours neighbours in the BCC crystal crystal and 2.54Å when it has 12 nearest nearest neighbours neighbours in the FCC crystal.
- If the inter-ionic separation is fixed, it means the atoms are stationary, and this can occur only at 0 Kelvin. Therefore the atoms are at their minimum energy E 0 , and inter-ionic separation r 0, at 0 Kelvin. The minimum energy E 0, and equilibrium inter-ionic spacing r 0, at 0 Kelvin.
- The solid Effect of increasing temperature on the vibration of the ions and hence on the inter-ionic separation becomes consistent with the higher temperatures by having the ions gain energy, and vibrate with increased amplitudes.

- Ideal Crystals → Real Crystals → Microstructures → Material → Component
- Crystal
- A 3D translationally periodic arrangement of atoms in a space is called a crystal.
- Lattice
- A 3D translationally periodic arrangement of points in a space is called a crystal.

- Crystal = Lattice (Where to repeat)+Motif (What to repeat)

Cubic space lattices

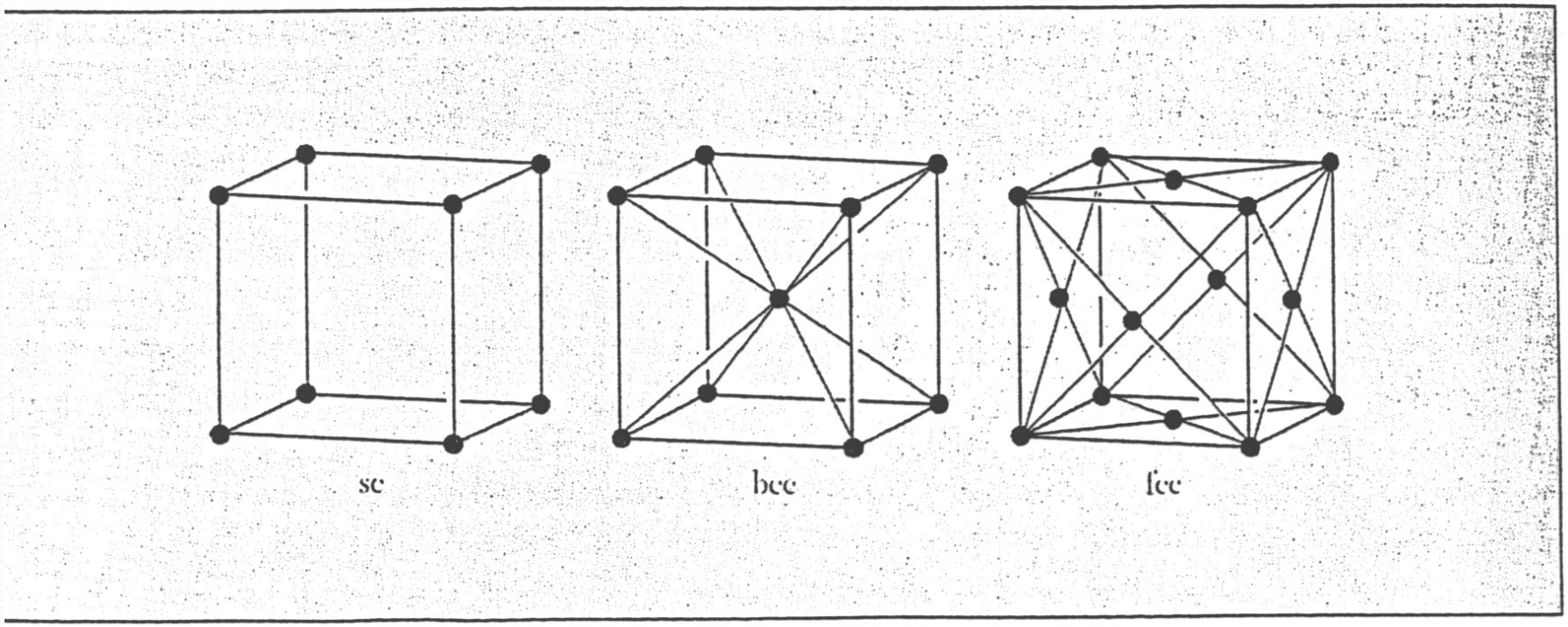
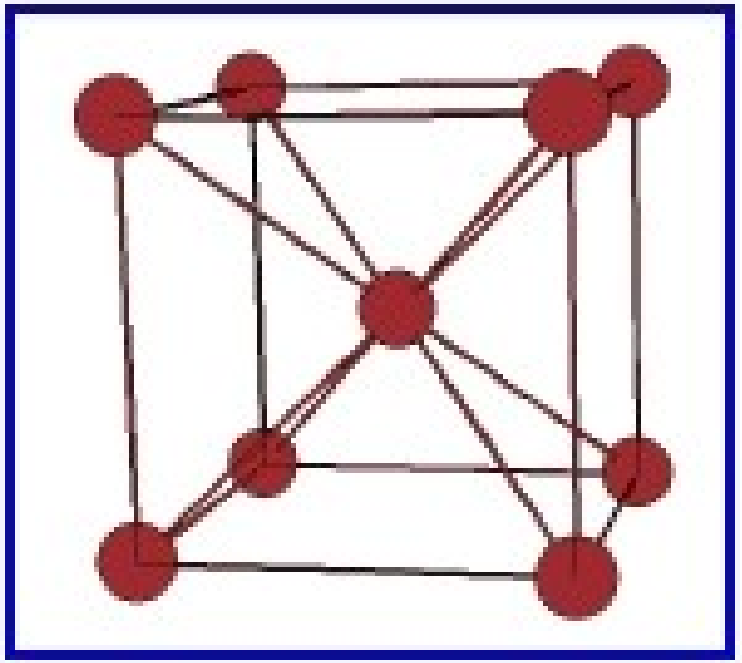


Figure 10 The cubic space lattices. The cells shown are the conventional cells.

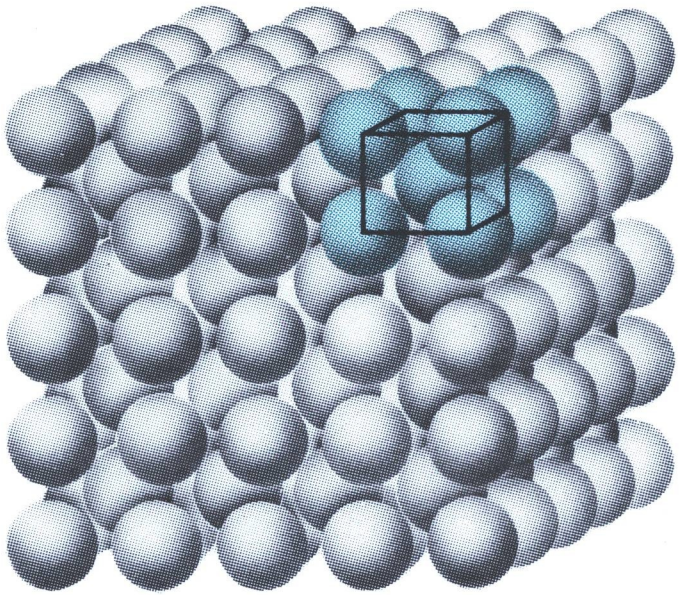
BCC Structure



Body Centered Cubic
and related structures

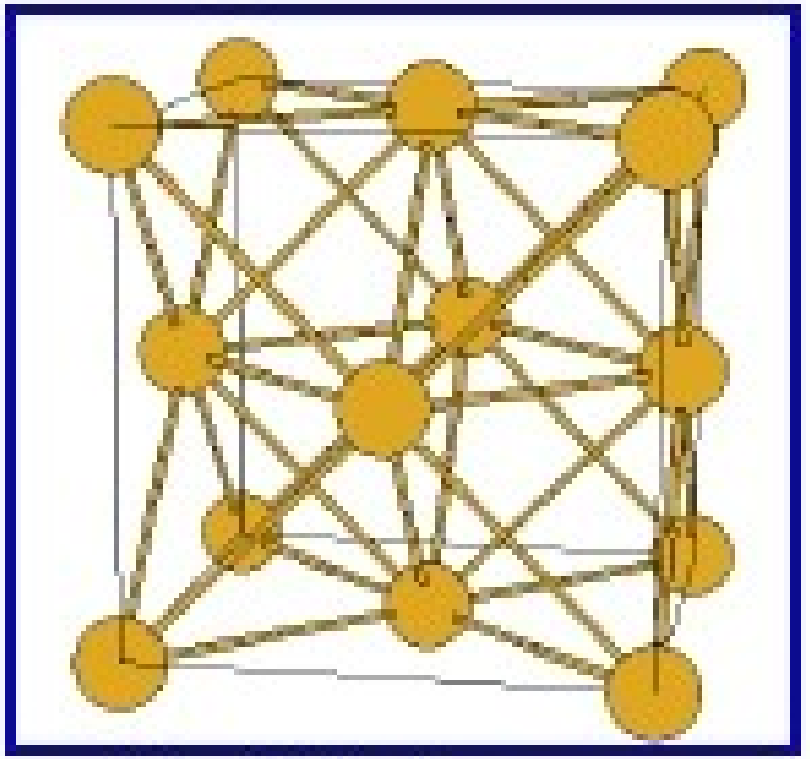
BCC Crystal

(a) (b)



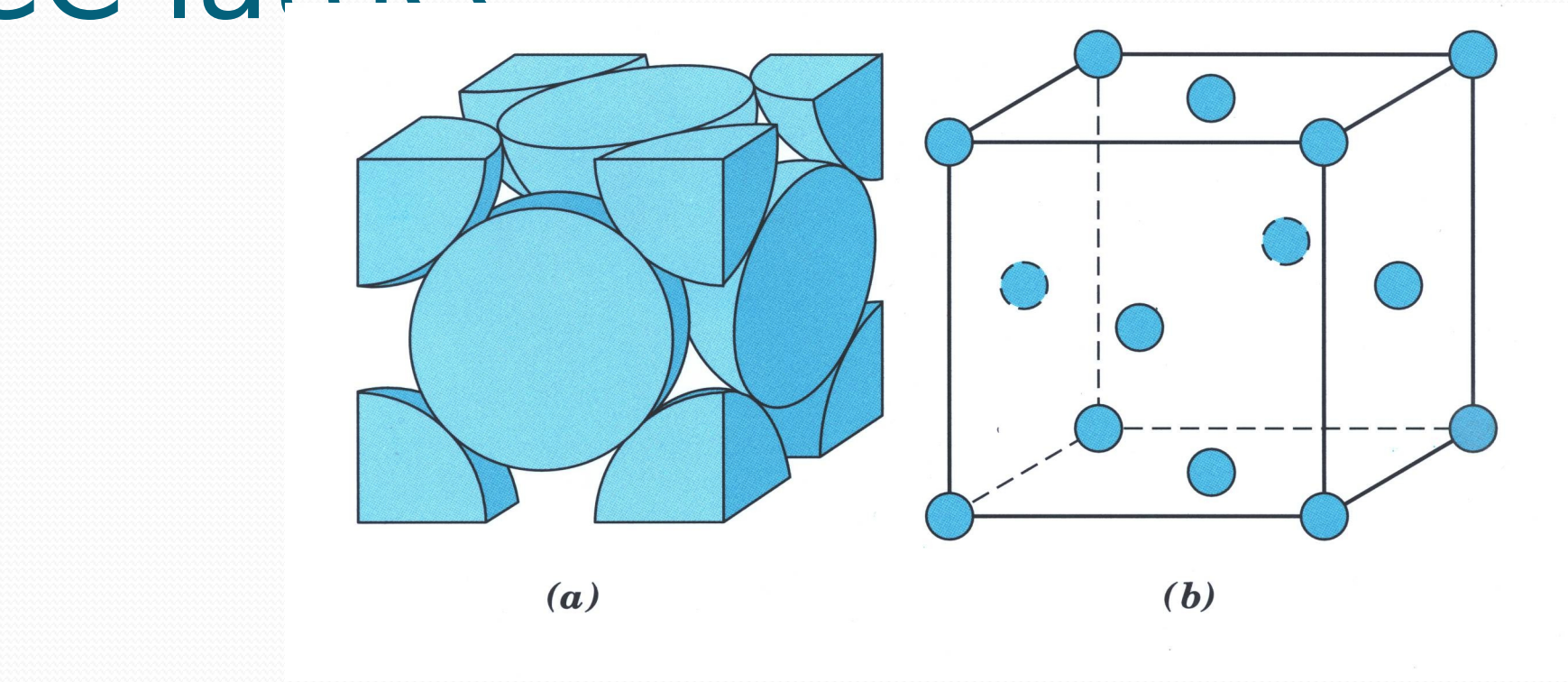
(c)

FCC Structure

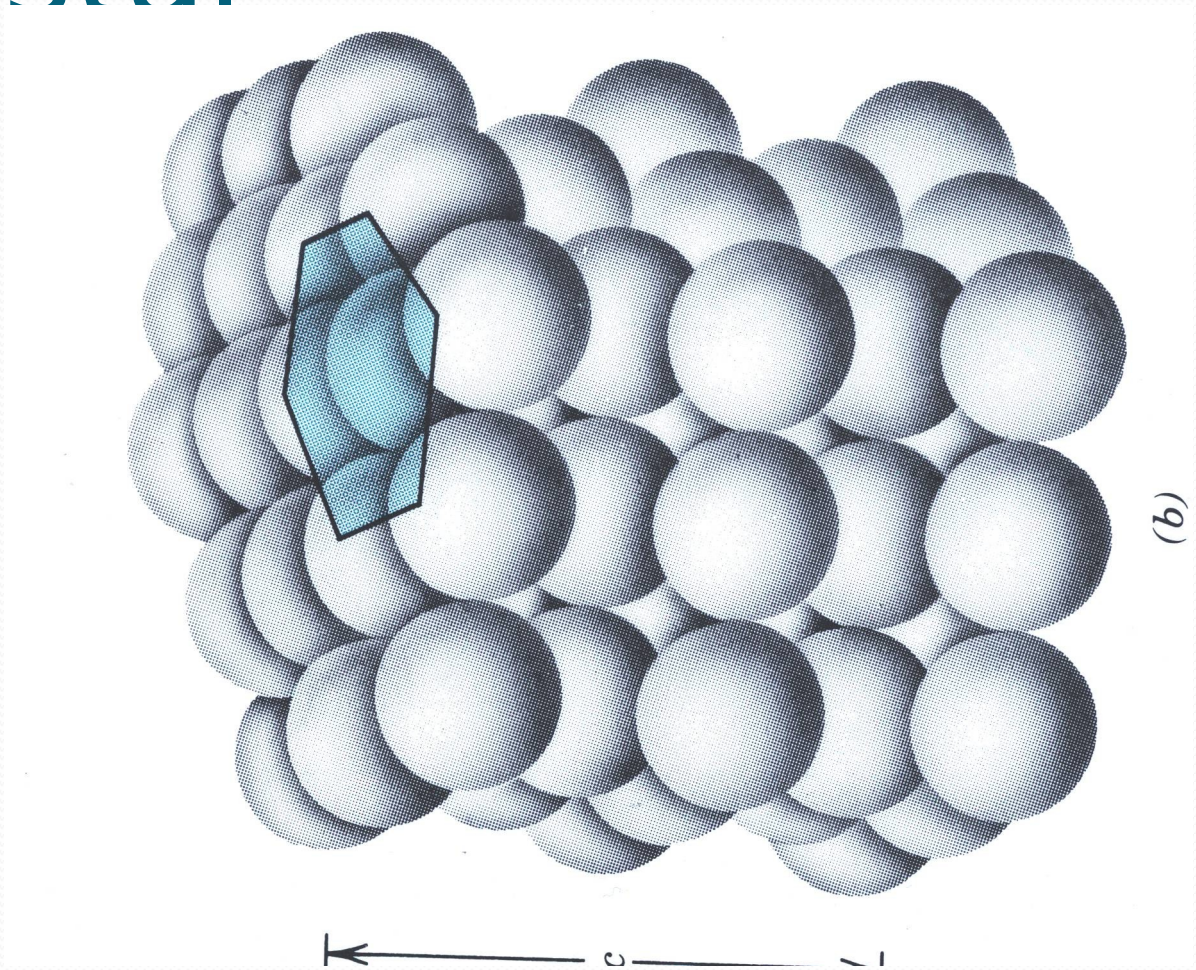


A1 (fcc) Structure

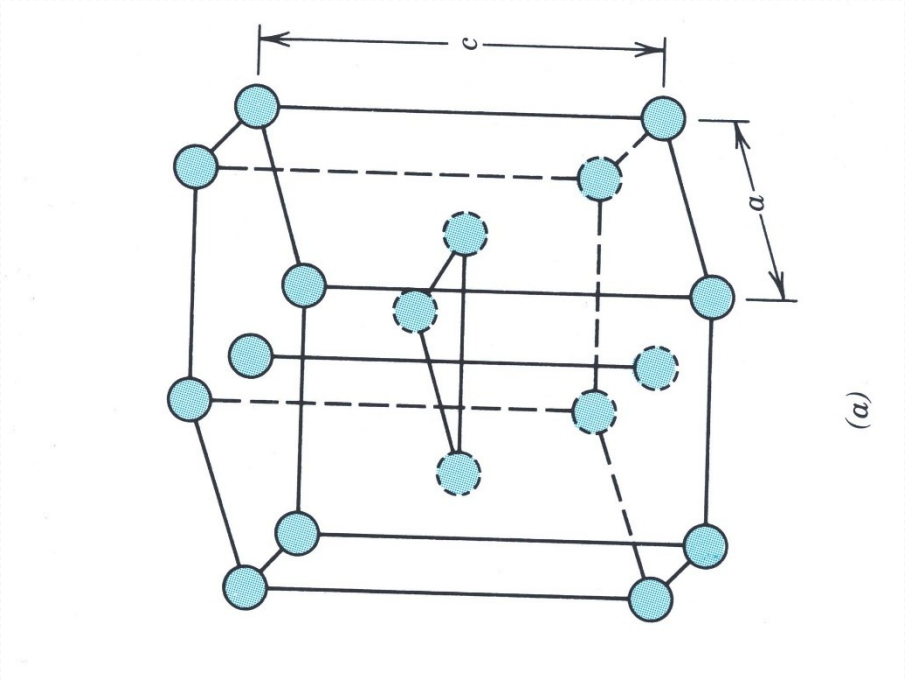
FCC lattice



HCP Crystal

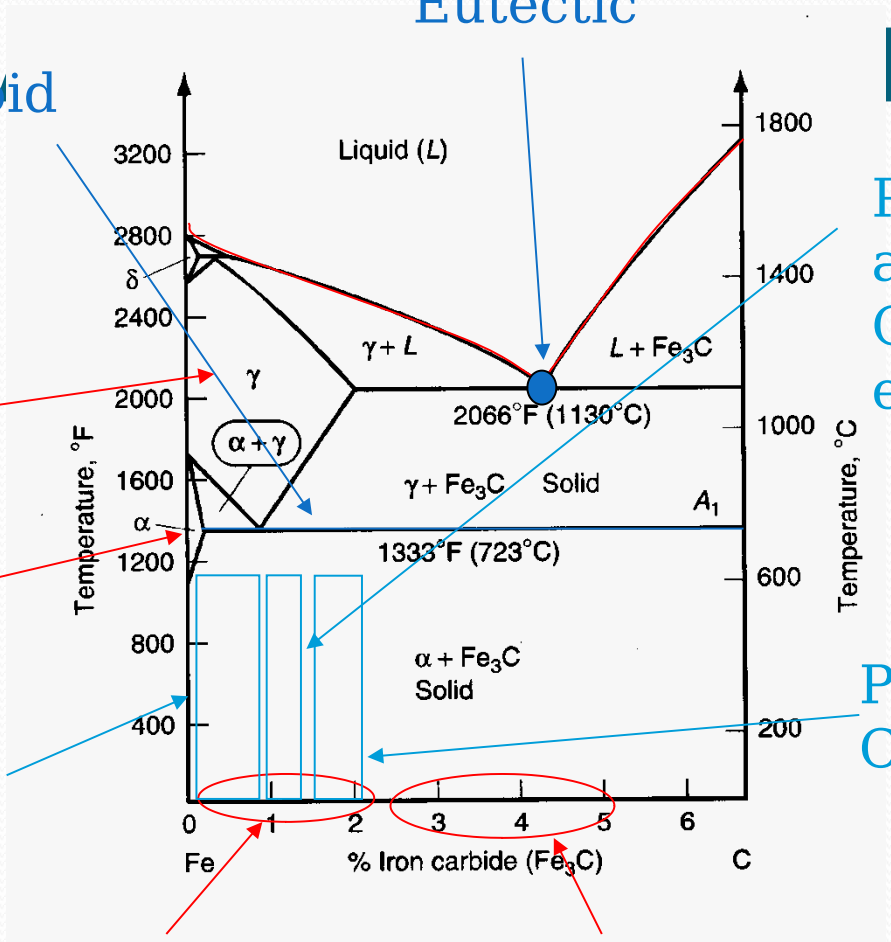


HexagonalClosePacked



HCP lattice is not a Bravais lattice, because orientation of the environment
Of a point varies from layer to layer along the c-axis.

IRON IRON-C M



Eutectic

eutectoid

Austenite

Ferrite

Pearlite

Pearlite and Cementite

Pearlite and Carbide

Steel

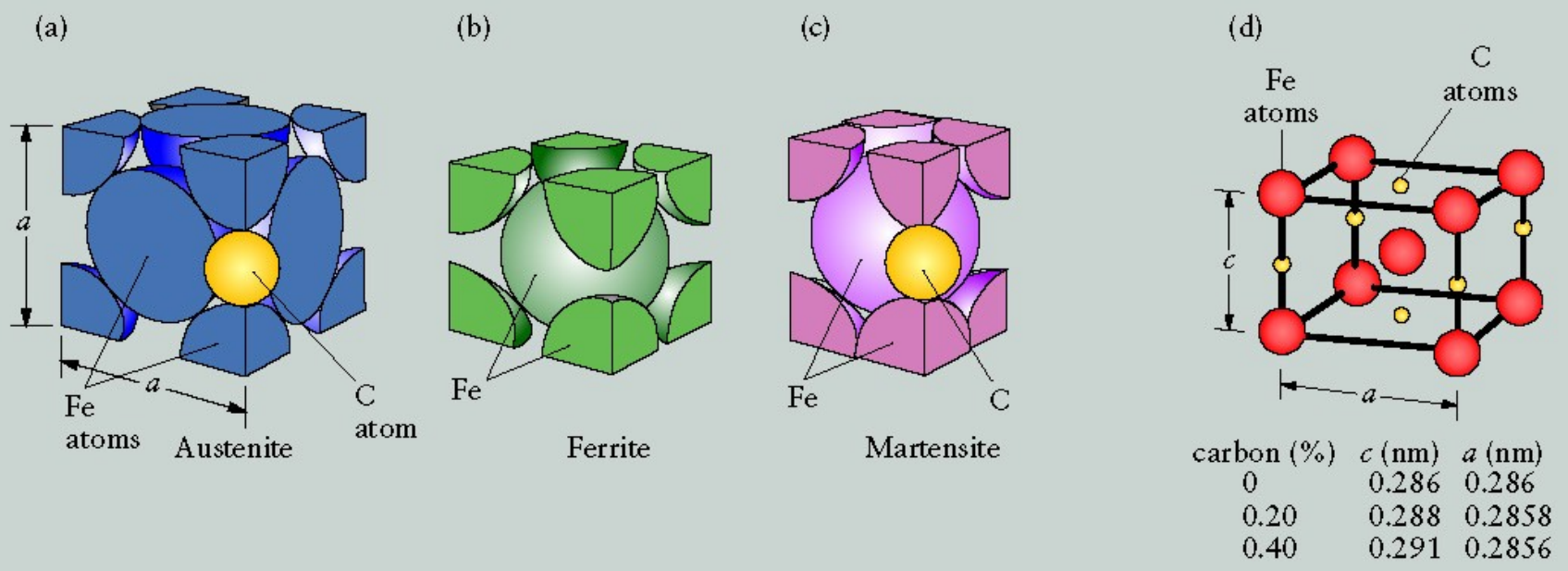
Cast iron

Definition of structures

Various phases that appear on the Iron-Carbon equilibrium phase diagram are as under:

- Austenite
- Ferrite
- Pearlite
- Cementite
- Martensite*
- Ledeburite

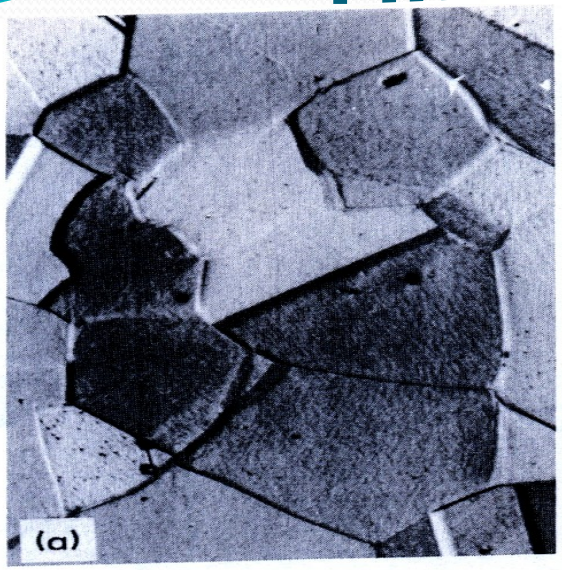
Unit Cells of Various Metals

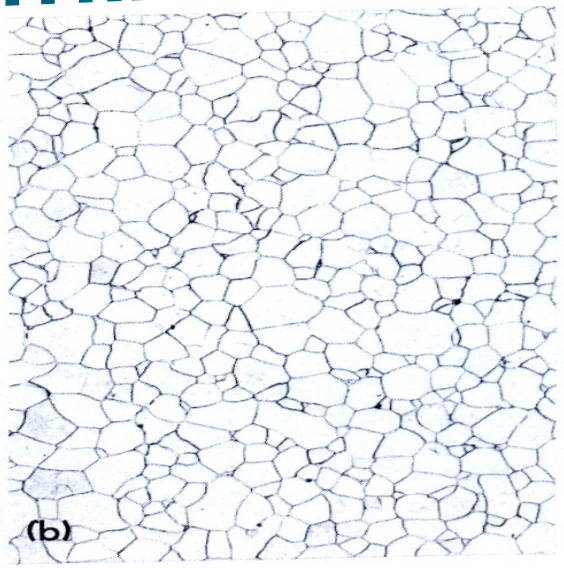


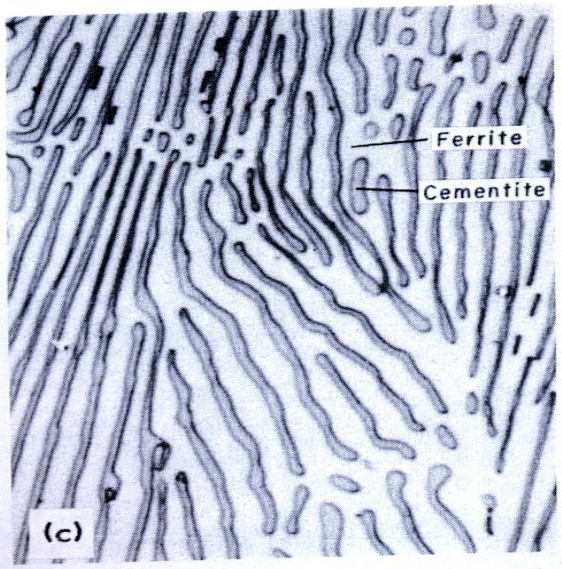
carbon (%)	c (nm)	a (nm)
0	0.286	0.286
0.20	0.288	0.2858
0.40	0.291	0.2856

- FIGURE - The unit cell for (a) austentite, (b) ferrite, and (c) martensite. The effect of the percentage of carbon (by weight) on the lattice dimensions for martensite is shown in (d). Note the interstitial position of the carbon atoms and the increase in dimension c with increasing carbon content. Thus, the unit cell of martensite is in the shape of a rectangular prism.

Microstructure of different phases of steel







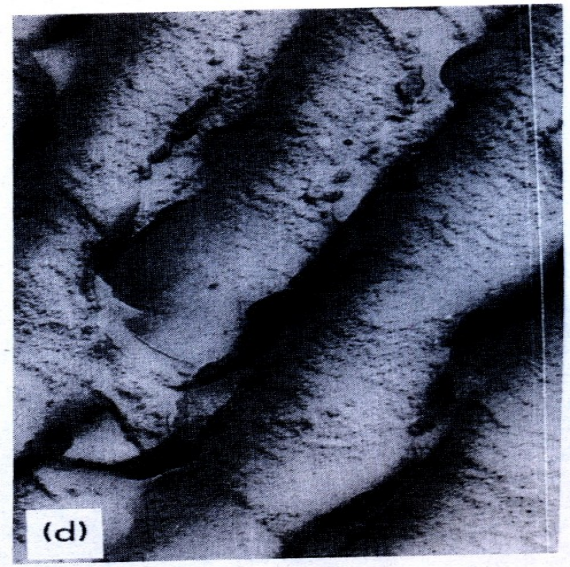
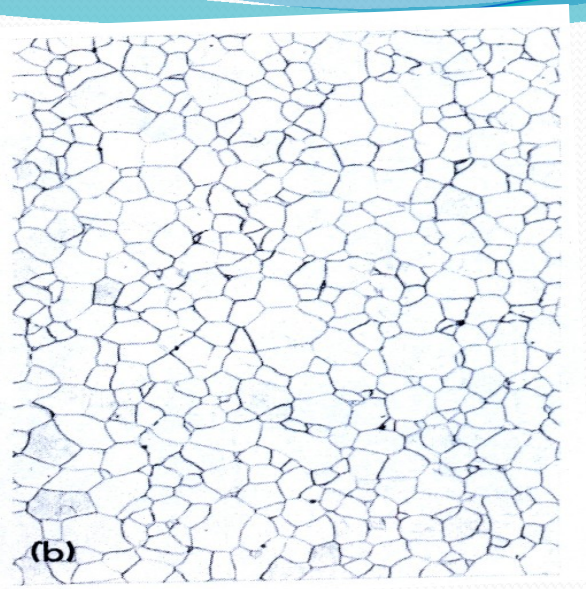


Fig. 7·8 The microstructure of (*a*) austenite, 500X; (*b*) ferrite, 100X; (*c*) pearlite, 2,500X; (*d*) pearlite, electron micrograph, 17,000X; enlarged 3X in printing. (*a*, *b*, and *c*, Research Laboratory, U.S. Steel Corporation.)

Definition of structures

- **Ferrite** is known as α solid solution.
- It is an interstitial solid solution of a small amount of carbon dissolved in α (BCC) iron.
- stable form of iron below 912 deg.C
- The maximum solubility is 0.025 % C at 723°C and it dissolves only 0.008 % C at room temperature.
- It is the softest structure that appears on the diagram.

Definition of structure:



Ferrite

- Average properties are:
  - Tensile strength = 40,000
  - Elongation = 40 % in 2 in;
  - Hardness > Rockwell C 0

    or > Rockwell B 90

Definition of structures

- **Pearlite** is the eutectoid mixture containing 0.80 % C and is formed at 723°C on very slow cooling.
- It is a very fine platelike or lamellar mixture of ferrite and cementite.
- The white ferritic background or matrix contains thin plates of cementite (dark).

Definition of structures

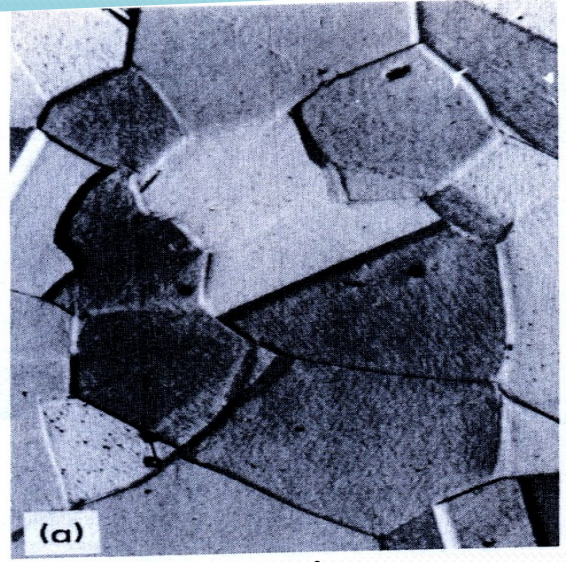
Pearlite

- Average properties are:
  - Tensile strength = 120,000 psi;
  - Elongation = 20 % in 2 in.;
  - Hardness = Rockwell C 20, Rock well B 95-100, or BHN 250-300.

Definition of structures

- **Austenite** is an interstitial solid solution of Carbon dissolved in γ (F.C.C.) iron.
- Maximum solubility is 2.0 % C at 1130°C.
- High formability, most of heat treatments begin with this single phase.
- It is normally not stable at room temperature. But, under certain

Definition of structure



Austenite

- Average properties are:
  - Tensile strength = 150,000 psi;
  - Elongation = 10 percent in 2 in.;
  - Hardness = Rockwell C 40, approx; and
  - toughness = high

Definition of structures

- **Cementite** or iron carbide, is very hard, brittle intermetallic compound of iron & carbon, as Fe_3C, contains 6.67 % C.
- It is the hardest structure that appears on the diagram, exact melting point unknown.
- Its crystal structure is orthorhombic.
- It is has
  - low tensile strength (approx. 5,000 psi), but

Definition of structures

- **Ledeburite** is the eutectic mixture of austenite and cementite.
- It contains 4.3 percent C and is formed at 1130°C.

Definition of structures

- **Martensite** - a super-saturated solid solution of carbon in ferrite.
- It is formed when steel is cooled so rapidly that the change from austenite to pearlite is suppressed.
- The interstitial carbon atoms distort the BCC ferrite into a BC-tetragonal structure (BCT).- responsible for the hardness of quenched steel

The Iron-Iron Carbon Diagram

- A map of the temperature at which different phase changes occur on very slow heating and cooling in relation to Carbon, is called Iron- Carbon Diagram.
- Iron- Carbon diagram shows
  - the type of alloys formed under very slow cooling,
  - proper heat-treatment temperature and
  - how the properties of steels and cast irons can be radically changed by heat-treatment.

Various Features of Fe-C diagram

Phases present

L

δ
BCC structure
Paramagnetic

α ferrite
BCC structure
Ferromagnetic
Fairly ductile

γ austenite
FCC structure
Non-magnetic
ductile

Fe_3C cementite
Orthorhombic
Hard
brittle

Reactions

Peritectic L + δ = γ

Eutectic L = γ + Fe_3C

Eutectoid γ = α + Fe_3C

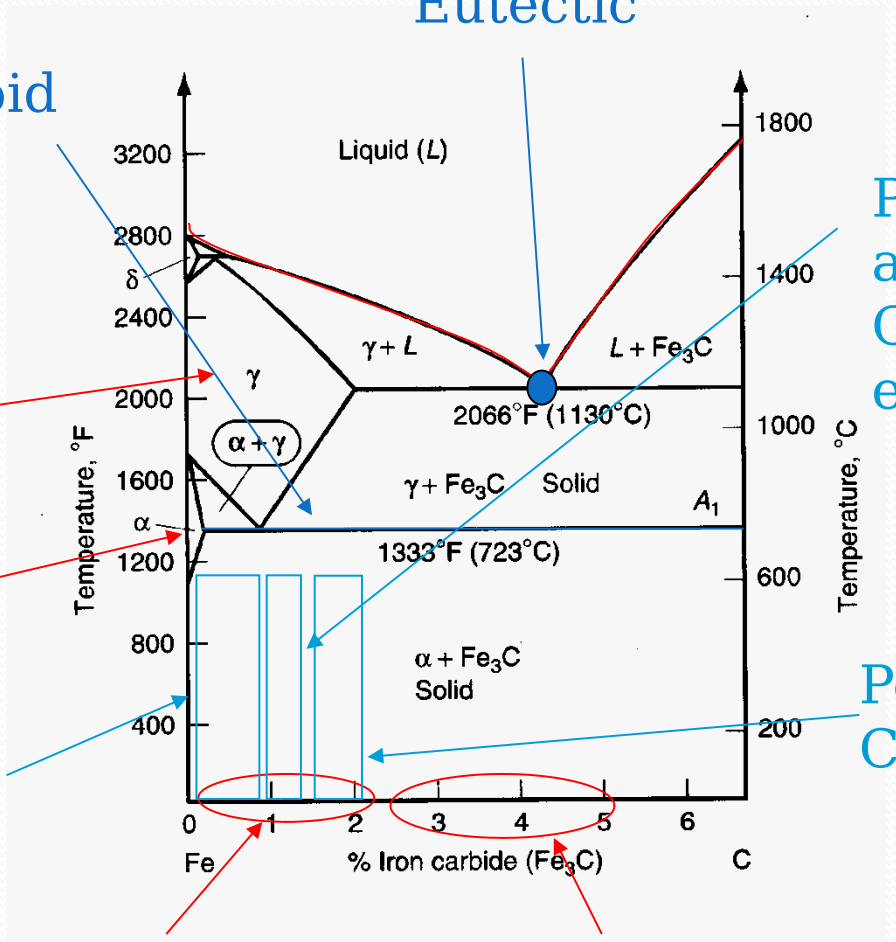
Max. solubility of C in ferrite=0.022%

Max. solubility of C in

Three Phase Reactions

- Peritectic, at 1490 deg.C, with low wt% C alloys (almost no engineering importance).
- Eutectic, at 1130 deg.C, with 4.3wt% C, alloys called cast irons.
- Eutectoid, at 723 deg.C with eutectoid composition of 0.8wt% C, two-phase mixture (ferrite & cementite). They are steels.

How to read the Fe-C phase diagram



Eutectic

eutectoid

Austenite

Ferrite

Pearlite

Pearlite and Cementite

Pearlite and Carbide

Steel

Cast iron

The Iron-Iron Carbide Diagram

The diagram shows three horizontal lines which indicate isothermal reactions (on cooling / heating):

- First horizontal line is at 1490°C, where peritectic reaction takes place:

  Liquid + δ ↔ austenite

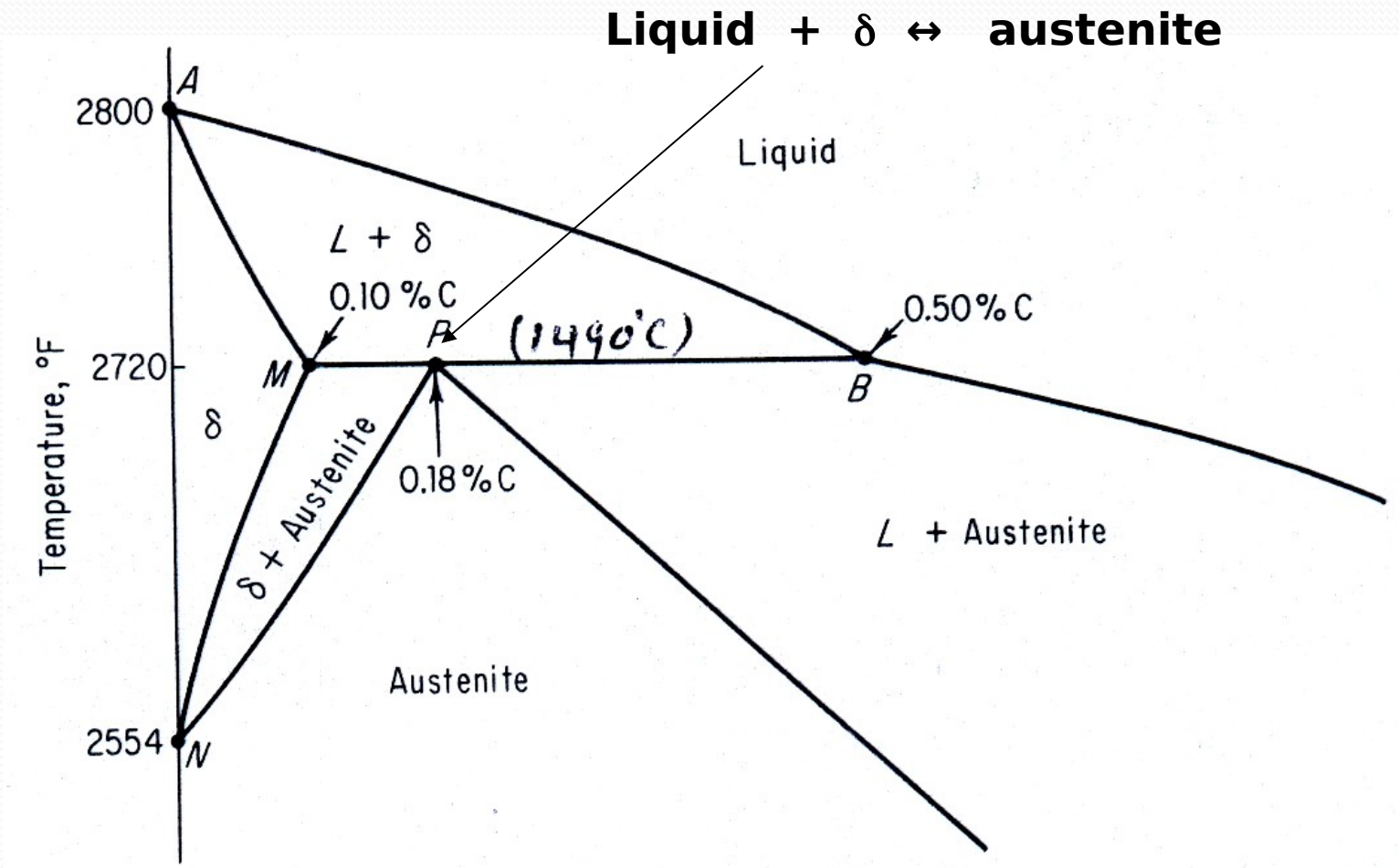
- Second horizontal line is at 1130°C, where eutectic reaction takes place:

  liquid ↔ austenite + cementite

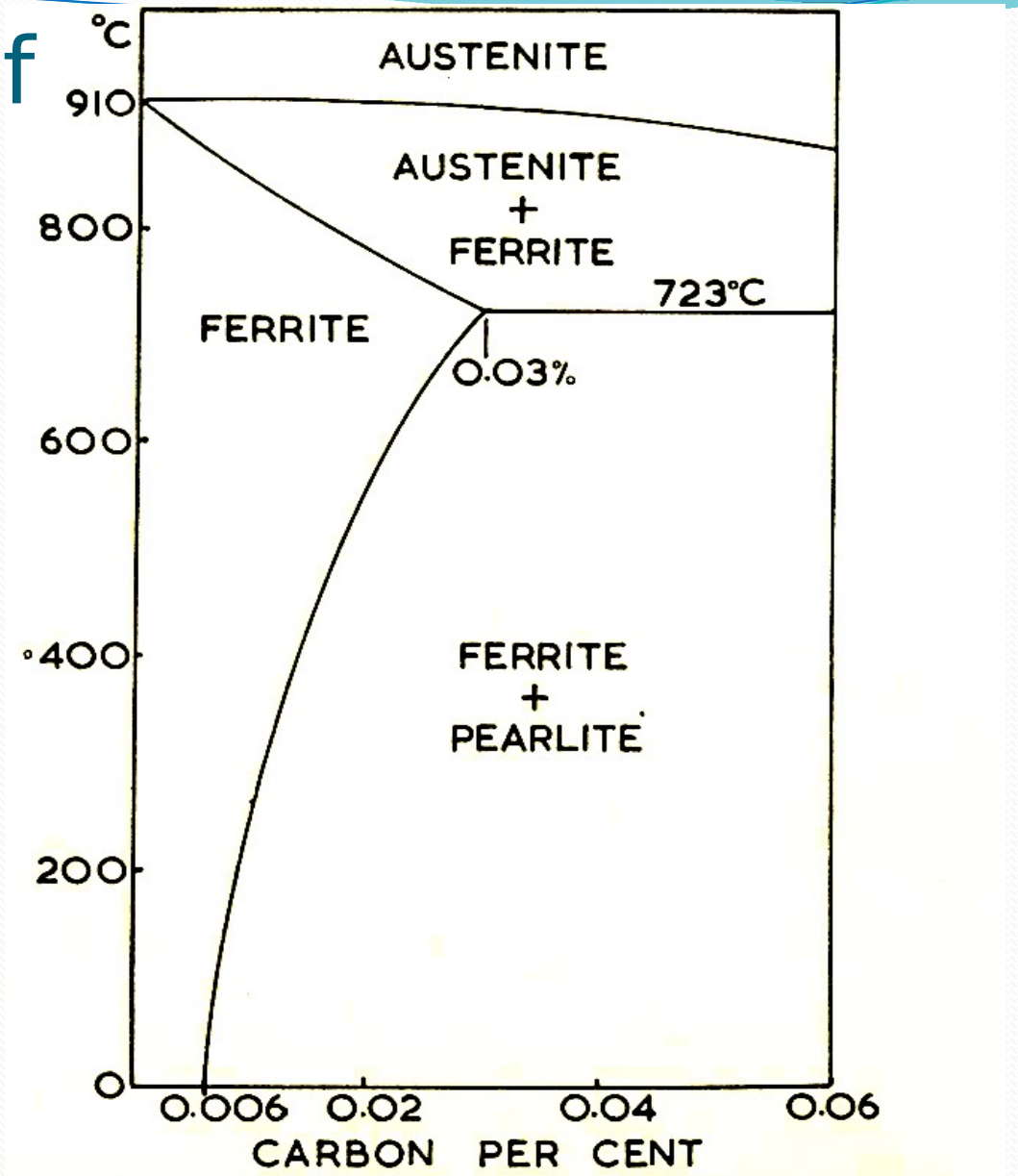
- Third horizontal line is at 723°C, where eutectoid reaction takes place:

  austenite ↔ pearlite (mixture of ferrite & cementite)

Delta region of Fe-Fe carbide diagram



Ferrite region of Fe-Fe Carbide diagram



2.—The "Ferrite Area" of the Iron–Carbon Equilibrium Diagram, Showing the Extent to Which Carbon is Soluble in α Iron.

The Austenite to ferrite / cementite transformation in relation to Fe-C diagram

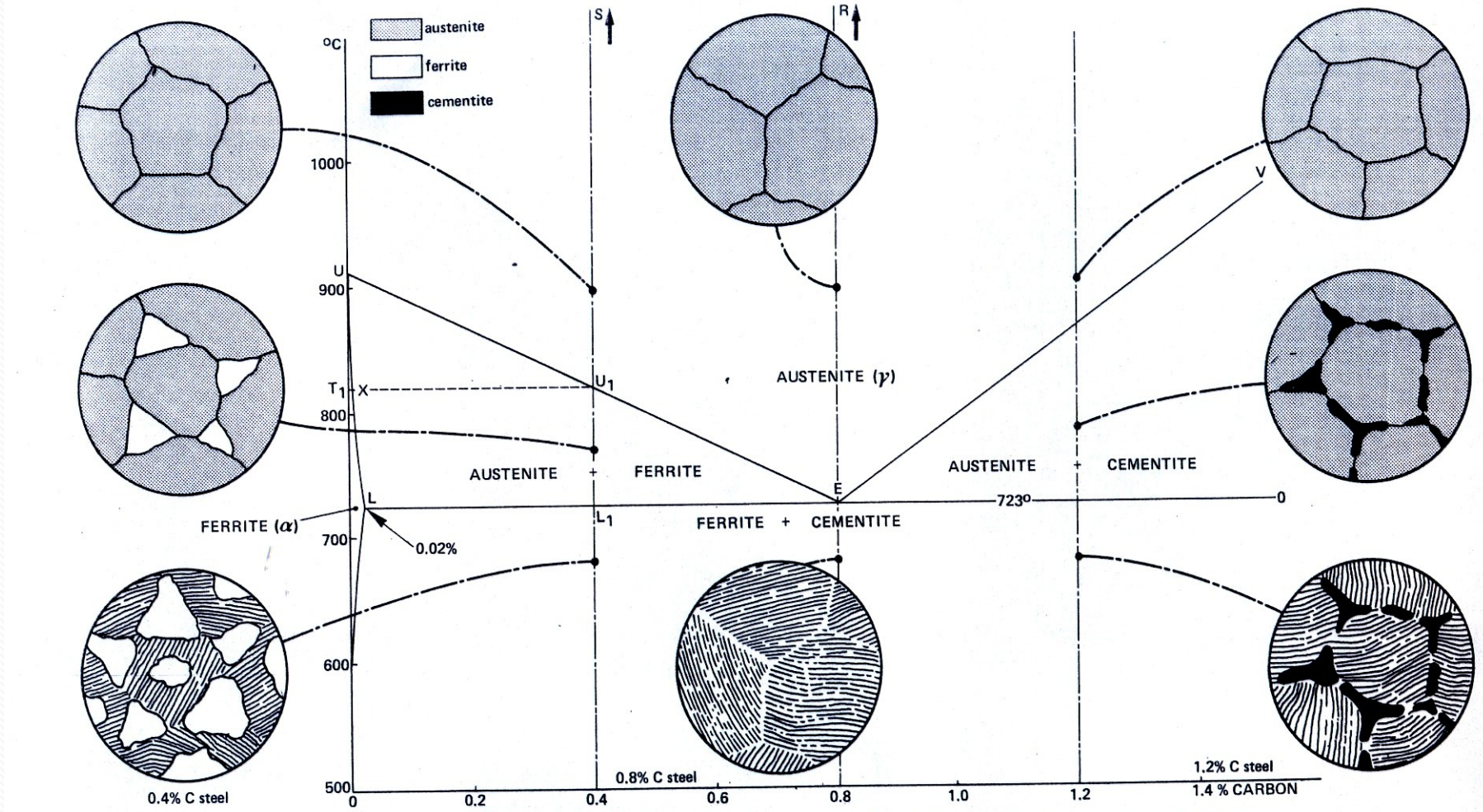


Fig. 9.3—The austenite → ferrite/cementite transformation in relation to the iron–carbon diagram.

The Austenite to ferrite / cementite transformation in relation to Fe-C diagram

In order to understand the transformation processes, consider a steel of the eutectoid composition. 0.8% carbon, being slow cooled along line *x-x'*.

- At the upper temperatures, only austenite is present, with the 0.8% carbon being dissolved in solid solution within the FCC. When the steel cools through 723°C, several changes occur simultaneously.

The Austenite to ferrite / cementite transformation in relation to Fe-C diagram

- The iron wants to change crystal structure from the FCC austenite to the BCC ferrite, but the ferrite can only contain 0.02% carbon in solid solution.
- The excess carbon is rejected and forms the carbon-rich intermetallic known as cementite.

Strengthening Mechanisms

- The ability of a metal to deform depends on the ability of the dislocations to move and the slip of dislocations weakens the crystal.
- Hence we have two strategies to strengthen the crystal/material: completely remove dislocations → difficult, but dislocation free whiskers have been produced (however, this is not a good strategy as dislocations can nucleate during loading) Increase resistance to the motion of dislocations or put impediments to the motion of dislocations → this can be done in many ways as listed below.

Solid Solution Strengthening

- The introduction of solute atoms into solid solution in the solvent-atom lattice invariably produces an alloy which is stronger than the pure metal
- Two types of solid solutions:

Substitutional solid solutions → Solute atoms occupy lattice points in the solvent lattice (Hume Rothery's rules are to be satisfied)

Interstitial solid solutions → Solute atoms occupy interstitial positions in the solvent lattice (Carbon, Nitrogen, Boron, Oxygen, Hydrogen are the common interstitial solutes)

- The stress fields around solute atoms interact interact with the stress fields around the dislocation.
- This interaction provides frictional resistance to dislocations motion and static locking of dislocations
- The factors playing an important role on strengthening effect: Size of the solute Concentration of solute Elastic modulus of the solute (higher the elastic modulus of the solute greater the strengthening effect) Nature of distortion produced by solute atoms (Spherical or Non-spherical)

Effect of Size and Concentration of Solute

- Size effect depends on:

  1) Size difference - For the same size difference the smaller atom gives a greater strengthening effect

  2) Concentration of the solute (c) -(c y ∝ ~ σ)

- More the size For the same size difference the smaller atom gives a greater strengthening effectdifference, more the intensity of stress field around solute atoms and more is the hardening effect.
- Large the concentration difference, more obstacles to dislocations motion and strength increases (Increase in σY is proportional to concentration of the solute).

Relative strengthening effect of Interstitial and Substitutional atoms

- Interstitial solute atoms have a non-spherical distortion field and can elastically interact with both edge and screw dislocations. Hence they give a higher hardening effect (per unit concentration) as compared to substitutional atoms which have (approximately) a spherical distortion field

Hardening of Precipitates

- Precipitates may be coherent, semi-coherent or incoherent. Coherent (& semi-coherent) precipitates are associated with coherency stresses.
- Dislocations cannot glide through incoherent precipitates.
- Inclusions behave similar to incoherent precipitates in this regard (precipitates are part of the system, whilst inclusions are external to the alloy system).
- A pinned dislocation (at a precipitate) has to either climb over it (which becomes favourable at high temperatures) or has to bow around it.

Orowan bowing mechanism : Pinning effect

- Dislocations can bow around widely separated inclusions. In this process they leave dislocation loops around the inclusions, thus leading to an increase in dislocation density. This is known as the Orowan bowing mechanism as shown in the figure below.
- The next dislocation arriving (similar to the first one), feels a repulsion from the dislocation loop and hence the stress required to drive further dislocations increases. Additionally, the effective separation distance

Precipitate Hardening effect

- The hardening effect of precipitates can arise in many ways as below:
- Lattice Resistance: the dislocation may face an increased lattice friction stress in the precipitate.
- Chemical Strengthening: arises from additional interface created on shearing
- tacking-fault Strengthening: due to difference between stacking-fault energy between particle and matrix when these are both FCC or HCP (when dislocations are split into partials)
- Modulus Hardening: due to difference difference in elastic elastic moduli of the matrix and particle particle
- Coherency Strengthening: due to elastic coherency strains surrounding the particle Order Strengthening: due to additional work required to create an APB in case of dislocations passing through precipitates which have an ordered lattice

Strengthening by Dispersoids

- In dispersion hardening, the hard particles are mixed with matrix powder and consolidated and processed by powder metallurgy techniques.
- Example: Thoria dispersed Nickel → Fine particles of Thoria are dispersed in the nickel matrix and the inter particle distance is enough to hinder the dislocation movement thereby increasing the strength up to 0.9 times T m (T m in 0C).
- In dispersion hardening, dispersoids are incoherent with the matrix and dislocations cannot glide through these dispersoids and gets pinned.
- A pinned dislocation (at a precipitate) has to either climb over it (which becomes favorable at high temperatures) or has to bow around it (Orowan's Mechanism of Direction of Dislocation Motion Dislocation Dispersoid Dislocation Loop favorable at high temperatures) or has to bow around it (Orowan's Mechanism of Dispersion Hardening)
- Dislocation loop exert a back stress on dislocation which needs to be overcome for additional slip to take place and this causes hardening

Strain Hardening : Forest Dislocations

- What causes Strain hardening? → multiplication of dislocations
- Annealed material + Cold Work = Stronger material
- It is difficult to obtain crystals without dislocations (under special conditions whiskers have been grown without dislocations).
- Dislocation can arise by/form: Solidification (errors in the formation of a perfect crystal lattice) Plastic deformation (nucleation and multiplication) Irradiation
- High stresses
  - ► Heterogeneous nucleation at second phase particles
  - ► During phase transformation
- Frank-Read source Some specific sources/methods of formation/multiplication of dislocations include
- Orowan bowing mechanism

Strain hardening

- We had noted that stress to cause further plastic deformation (flow stress) increases with strain → strain hardening.
- This happens at Dislocations moving in non-parallel slip planes can intersect with each other
- → results in an increase in stress required to cause further plastic deformation
- ⇒ Strain Hardening / work hardening

One such mechanism by which the dislocation is immobilized is the LomerCottrell barrier

Strengthening by Grain Boundary

- Grain boundary is the boundary between two grains in a polycrystalline aggregate and this is the region of a disturbed lattice which is of few atomic diameters distance.
- There are two important ways in which grain boundary acts as a barrier to the dislocation Difficulty for a dislocation

> To pass through two different grain orientations (need to change the direction)

> The atomic disorder within a grain boundary region contributes to a discontinuity of slip planes from one grain to other.

Hall – Petch Relation

- A fine grained material is harder and stronger than one that is coarse grained since greater amounts of grain boundaries in the fine grained materials impede dislocation motion.
- The general relationship between yield stress (tensile strength) and grain size was proposed by Hall and Petch, which is known as Hall-Petch relation.
- σ Yield = σ o + k y $d^{-1/2}$
- Where, σyield = Yield stress
- σo = Friction stress or resistance to dislocation motion
- ky = Locking parameter or the hardening contribution from the grain boundary
- d = Grain diameter

Hot Working

- Plastic deformation which is carried out under conditions of temperature and strain rate such that recovery processes occur substantially so that large strains can be achieved with essentially no strain hardening.
- Normally performed at temperature >0.6Tm & at high strain rates in the range of 0.5-500 s-1

Advantages of Hot Working

- Larger deformation can be accomplished and more rapidly by hot working since the metal is in plastic state.
- Porosity of the metal is considerably minimized.
- Concentrated impurities, if any in the metal are disintegrated and distributed throughout the Disadvantages of Hot Working
- Concentrated impurities, if any in the metal are disintegrated and distributed throughout the metal.
- Grain structure of the metal is refined and physical properties is improved.
- No residual stresses in the material

Hot Working

- Poor surface finish and loss of metal due to rapid oxidation or scale formation on the metal surface
- Close tolerances cannot be maintained.
- It involves excessive expenditure on account of high cost of tooling. This, however, is compensated by the high production rate and better quality of products.

Warm Working

- Warm working is the plastic deformation of a meta at temperature below the temperature range of recrystallization and above the room temperature i.e. intermediate to hot and cold working.
- Advantages Compared to Hot Working

Combines the advantages of both hot and cold working into one operation. Fewer number of annealing operation (because of less strain hardening) Lesser loads on tooling and equipment Greater metal ductility

- Advantages compared to Cold Working

Improved dimensional control,

Lower energy costs.

Better precision of components

Lesser scaling and decarburization on parts

Better surface finish

Lesser thermal shock on tooling

Lesser thermal fatigue to tooling, and so greater life of tooling.

Cold Working

- Plastic deformation which is carried out in a temperature region and over a time interval such that the strain hardening is not relieved is called cold work. Normally performed at room temperature but in general < 0.3Tm, where recovery is limited and recrystallization does not occur
- Advantages of Cold Working
- Due to work hardening Strength and hardness of the metal are increased.
- It is an ideal method for increasing hardness of those metals which do not respond to the heat treatment.
- Better dimensional dimensional control control is possible possible because because the reduction reduction in size is not much.
- Provide fine grain size and good surface finish (No oxidation takes place).
- Handling is easier because of low operating temperature.
- Directional properties can be imparted.

Cold Working

- Disadvantages of Cold Working

Only ductile metals can be shaped through cold working.

Over-working of metal results in brittleness and it has to be annealed to remove the same.

Subsequent heat treatment is mostly needed to remove the residual stresses set up during cold working.

Higher forces and heavier and more powerful equipment are required for deformation

During cold work the point defect density (vacancies, self interstitials…) and dislocation density increase. Typical cold working techniques are rolling, forging, extrusion etc.

Cold working is typically done on ductile metals (e.g. Al, Cu, Ni)

Recovery, Recrystallization & Grain Growth

- Plastic deformation in the temperature range (0.3 Plastic deformation in the temperature range (0.3 – 0.5) Tm → COLD WORK
- Point defects and dislocations have strain energy associated with them
- (1 -10) % of the energy expended in plastic deformation is stored in the form of strain energy (in these defects) → The material becomes battery of energy..!
- The cold worked material is in a micro structurally metastable state.
- Depending on the severity of the cold work the dislocation density can increase 4-6 orders of magnitude more. The material becomes stronger, but less ductile.
- The cold worked material is stronger (harder), but is brittle.
- Heating the material (typically below 0.5T m) is and holding for sufficient time is a heat treatment process called annealing.
- Depending on the temperature of annealing processes like Recovery at lower temperatures) or Recrystallization (at higher temperatures) may take place. During these processes the material tends to go from a micro structurally metastable state to a lower energy state (towards a stable state).
- Further ‘annealing’ of the recrystallized material can lead to grain growth.

Overview of processes taking place during annealing of cold worked material and the driving force for these processes

- Cold work ->Anneal -> Recrystallization
- Recovery--- Driving force is free energy stored in point defects and dislocation.
- Recrystallization--- Driving force is free energy stored in dislocations
- Grain growth --- Driving force is free energy stored in grain boundaries

- With Cold Work, Changes occur to almost all physical and mechanical properties

↑ Strength ↑ Hardness ↑ Electrical resistance ↓ Ductility

Recovery

- Recovery takes place at low temperatures of annealing
- “Apparently no change in microstructure”
- Excess point defects created during Cold work are absorbed:
  - ► at surface or grain boundaries
  - ► by dislocation climb
- Random dislocations of opposite sign come together and annihilate each other
- Dislocations of same sign arrange into low energy configurations:
  - ► Edge → Tilt boundaries
  - ► Screw → Twist boundaries Recovery
- POLYGONIZATION
- Overall reduction in dislocation density is small
- At the early stage of annealing of cold formed metals, external thermal energy permits the dislocations to move and form the boundaries of a polygonized subgrain structure while the dislocation density stays almost unchanged.
- This process also removes the residual stresses formed due to cold working significant. The recovering of physical and mechanical properties varies with the temperature and time.

Recrystallization

- Trecrystallization ∈ (0.3 – 0.5) Tm
- “Nucleation” and growth of new, strain free crystals
- Nucleation of new grains in the usual sense may not be present and grain boundary migrates into a region of higher dislocation density
- ΔG (recrystallization) = G (deformed material) – G (undeformed material)
- TRecrystallization is the temperature at which 50 % of the material recrystallizes in 1 hour

Direction of grain boundary migration would be

from Region of lower dislocation density to the Region of higher dislocation density

Recrystallisation

- Deformation ↑ ⇒ recrystallization temperature (Trecrystallization) ↓
- Initial grain size ↓ ⇒ recrystallization temperature ↓
- High cold work + low initial grain size ⇒ finer recrystallized grains
- ↑ cold work temperature ⇒ lower strain energy stored ⇒ ↑ recrystallization temperature
- Rate of recrystallization = exponential function of temperature
- Trecrystallization = strong function of the purity of the material Recrystallization Trecrystallization (very pure materials) ~ 0.3 Tm Trecrystallization (impure) ~ (0.5 – 0.6) Tm
- ► Trecrystallization (99.999% pure Al) ~ 75oC Trecrystallization (commercial purity) ~ 275oC
- The impurity atoms segregate to the grain boundary and retard their motion → Solute drag (can be used to retain strength of materials at high temperatures)
- Second phase particles also pin down the grain boundary during its migration

Hot Work and Cold Work

- Recrystallization temperature is ~ 0.4 Tm
- Hot Work >> Plastic deformation above T-Recrystallization

  Hot Work − 0.7 Tm − 0.8 Tm − 0.9 Tm

  The lower limit of temperature for hot working is taken as 0.6 Tm

  When a metal is hot worked. The conditions of deformation are such that the sample is soft and ductile. The effects of strain hardening are negated by dynamic and static processes (which keep the sample ductile)
- Cold Work >> Plastic deformation below T-Recrystallization

  Cold Work − 0.3 Tm − 0.2 Tm − 0.1 Tm

  Upper limit ►0.3 Tm

  The effects of strain hardening is not negated. Recovery mechanisms involve mainly motion of point defects.
- Warm Work >> − 0.6 Tm − 0.7 Tm − 0.5 Tm − 0.4 Tm

Grain Growth

- Large grains have lower free energy than small grains. This is associated with the reduction of the amount of grain boundary.
- Therefore, under ideal conditions, the lower energy state for a metal would be as a single crystal. This is driving force for grain growth.

- Opposing this force is the rigidity of the lattice. As the temperature increases, the rigidity of the lattice decreases and the rate of grain growth is more rapid.
- At any given temperature there is a maximum grain size at which these two effects are in equilibrium
- Grain growth - ↓ Time at temperature↑
  - ↓ Degree of prior deformation ↑
  - ↓ Annealing temperature↓
    - ↓ Insoluble impurities↑
    - ↓ Heating Time↓

Materials Specifications Considerations

Materials Specification is an important component in the pipeline design

for fulfilling the stringent requirements with respect to :

- **Safety**
- **Quality**
- **Economy**
- **Reliability**
- **Productivity**
- **Operational Efficiency**
- **Credibility**

Requirements to be kept in mind for the line pipe material

- **The material should have high enough strength to use smaller wall thicknesses**
- **It should posses sufficiently high ductility easy processing.**
- **It should have sufficiently high toughness to resist crack propagation in service.**
- **Should have good weldability for shop fabrication and field welding.**
- **Should not require post weld eat treatment for good final properties.**
- **Should possess adequate atmospheric corrosion resistance.**
- **Should have appropriate corrosion resistance to the service fluid.**
- **Should yield itself for repair welding.**
- **Should be capable of being procured with relative ease.**
- **Should be capable of being produced in the form of choice.**

Knowledge requirements for Line pipe Material Selection

- **A good knowledge of the basics of Metallurgy.**
- **A good knowledge of the effects of alloying elements in steels.**
- **A knowledge of material manufacturing processes and procedures.**
- **A familiarity of the Code, Standard and specification requirements**
- **A knowledge of the various material testing requirements and NDT.**
- **A knowledge of Quality Assurance Practices and Quality Control requirements.**
- **Basic knowledge of Specification Writing Practices**
- **Knowledge of the limitations of various manufacturing routes.**
- **Familiarity with the Materials Performance related information.**
- **A good knowledge of the principles of corrosion**
- **A good knowledge of corrosion Control Practices**

History of Improvement of Pipeline Materials

Date	Event	Industry Reaction
1943	Discovery of ductile-brittle transition in carbon steels.	Introduction of 15 ft-lb Energy requirement into specifications for ship plate .
1954	Above characteristics considered relevant energy for pipelines	TÜV introduced 3.5 mkg/cm2. requirement For line pipe steels.
1960	Brittle fracture propagation of 13 km in	Development of Battelle drop weight tear test (DWTT)
1969	Propagating ductile fracture in non-brittle, supposedly crack resistant, material.	Introduction of minimum Charpy energy based on various fracture models.

History of Development of Pipeline Materials

Date	Event	Industry Reaction
1970	Proposed construction of Alaskan/ Canadian	Steel development frenzy centered on X- 80 and -69°C (-90°F) toughness
1972	HIC failure in X-65 BP pipeline in Ummshaif (Arabian) Gulf.	Introduction of BP test (NACE TM-02-84 [SolutionB]).
1974	Unpredictable fracture arrest in full scale. (CAGSL) tests Attributed to rich gas, separations, arrest modelling and revision of rolling ideas for high strength linepipe.	Introduction of crack arrestors, high hoop stress and faulty model
1978	Stress corrosion cracking failures in newly installed Australian and Canadian pipelines	Better metallurgical (hardness), improved external coatings, Improved operating practices .
1978	Molybdenum "shortage" and price escalation.	Mo designed out of X-70 steels Nb-Cr design introduced plus TMCP.
2009	Failure of pipelines under moving permafrost Alaska	Ultra low carbon bainitic steels with specific TMCP in schedules

History of Development of Pipeline Materials

Date	Event	Industry Reaction
1988/89	Vanadium price increase to $50/kilo	Vanadium eliminated from many steels. Mo and Cr+TMCP substituted.
1990	Development of deepwater oil and gas reserves and design of collapse-resistant SAW linepipe developed for. pipelines and TLP tendons as well as high strength (80 ksi) seamless risers.	Very heavy wall thickness (44 mm) Oman-India and Black Sea pipeline
1997	Need for very high pressure systems for Arctic developments in remote areas.	Ultra high strength (135 ksi UTS) steels considered and composite reinforcement of conventional steels introduced.
1998	Limit state, strain based designs introduced.	Better characterization of material behaviour and influence of manufacturing process and coating.
2005-2008	Very large vanadium and molybdenum price increase especially in China and USA.	Nb-Cr type steels redeveloped to eliminate molybdenum and vanadium
2012	Requirements for strain based design specified	Introduction of special

Major effects of alloying elements in High Strength Line Pipe Steels.

Element	(wt%)	Effect and reason of adding
C	(0.03 - 0.10)	Matrix strengthening (by precipitation).
Mn	(1.6 - 2.0)	Delays austenite decomposition during AcC; Substitutional strengthening effect; Decreases ductile to brittle transition temperature; Indispensable to obtain a fine-grained lower bainite .
Si	(up to 0.6)	Improvement in strength (solid solution).
Nb	(0.03 - 0.06)	Reduces temperature range in which recrystallization is possible between rolling passes; Retard recrystallization and inhibit austenite grain growth (improves strength and toughness by grain refinement).

Major effects of alloying elements in High Strength Line Pipe Steels.

Element (wt%) Effect and reason of adding

Ni (0.2 - 1.0) - Improves the properties of low-carbon steels without impairing field weldability and low temperature toughness;

- In contrast to Mg and Mo, Ni tends to form less hardened microstructural constituents detrimental to low temperature toughness In the plate (increases fracture toughness).

V (0.03 - 0.08) - Leads to precipitation strengthening during the tempering treatment;

- Strong ferrite strengthener.

Mo (0.2 - 0.6) - Improves hardenability and thereby promotes the formation of the desired lower bainite microstructure.

Ti (0.005 - 0.03) - Grain refinement by suppressing the coarsening of austenite grains (TiN)

- Strong ferrite strengthener;

- Fixes the free Ni (prevent detrimental effect of Ni on hardenability).

Use of combination of Micro-alloying Elements

- **Over the past few years the steelmakers have pursued some strategic alloying combinations to meet the increasing demands on strength and toughness without compromising weldability, namely :**

- **V+Mo+Nb: Produce secondary hardening by forming carbides, nitrides and carbonitrides;**

- **Ni+Mo: Effective addition of microstructure refinement by suppressing austenite recrystallization during controlled rolling and steel strengthening by precipitation hardening and enhancement of hardenability;**

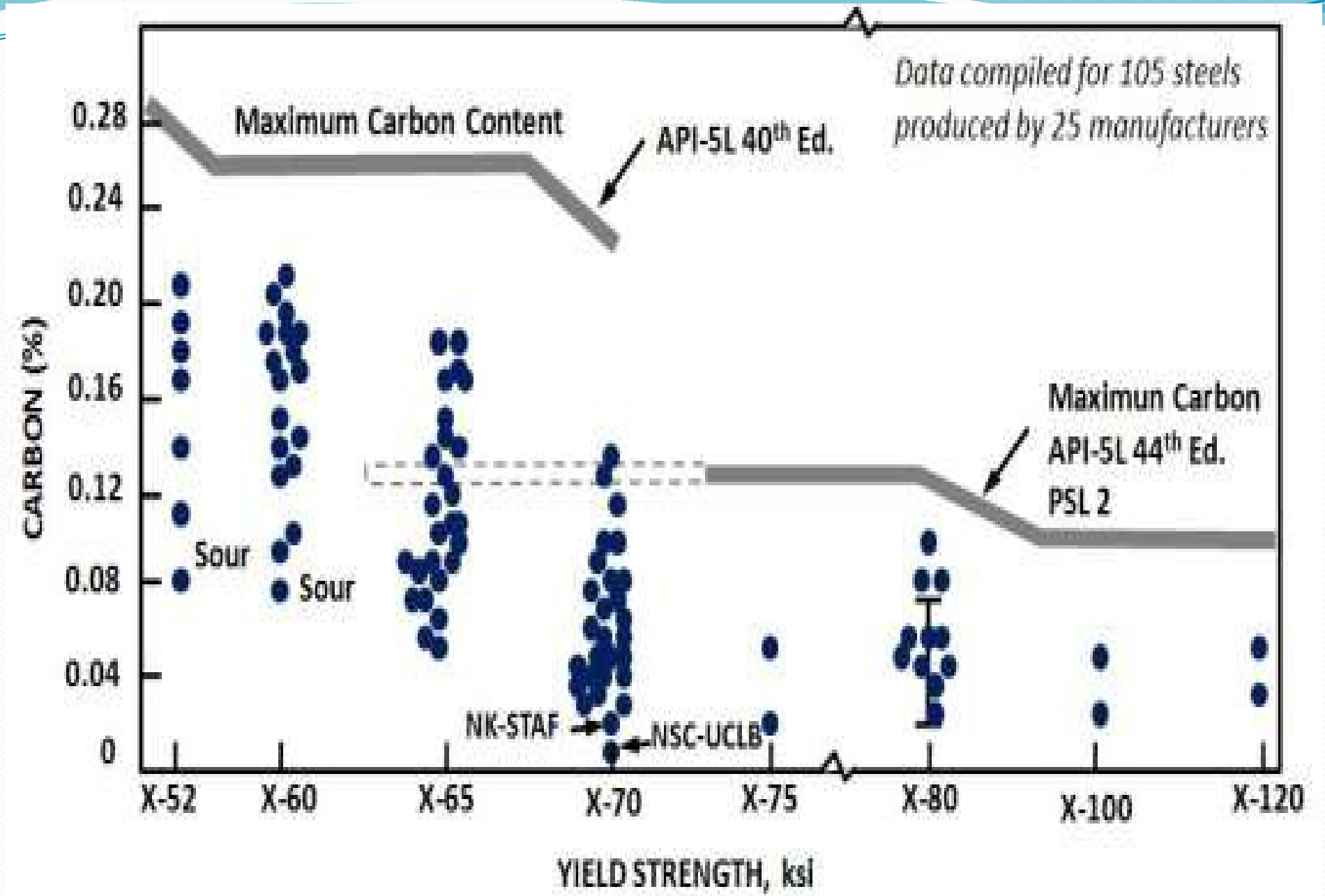
- **Ni+B: Synergistic improvement of hardenability;**

- **Nb+V: Increase strength properties. However, steels based on this combination may require relatively high carbon equivalent design, which can compromise the capability for preheat-free field welding;**

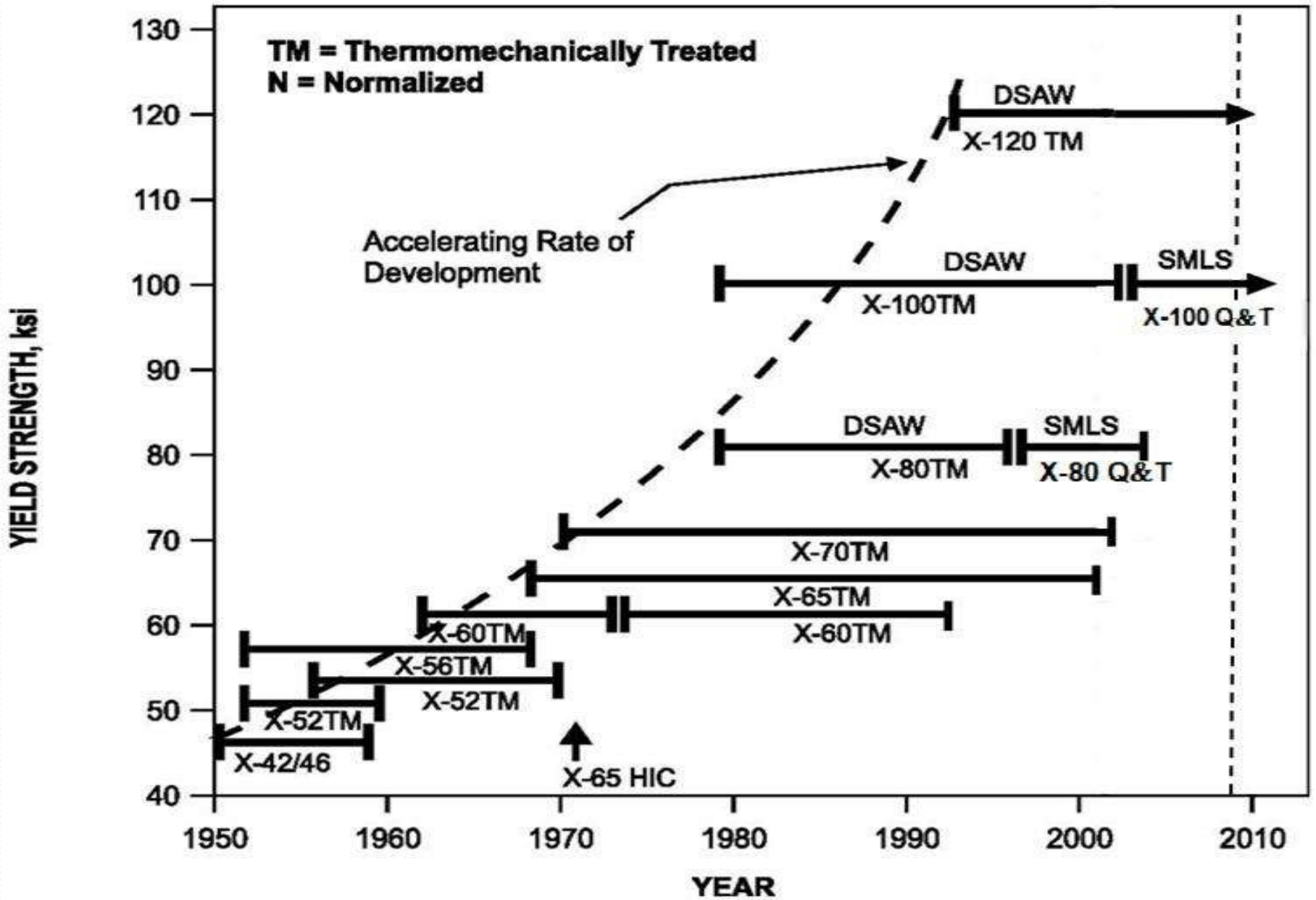
Use of combination of Micro-alloying Elements

- **Mo+Nb+Ti: - More effective (compared to the formerly applied Nb+V steels) in achieving the strength requirements of X70 and X80 (high Mn Steels) particularly in thicker pipe**
  - **A significantly finer ferrite grain size;**
  - **Low temperature transformation constituents such as bainite (B) containing accicular carbide needles in leaner alloyed X70 steels and martensite/austenite MA) in highly alloyed X80 steels;**
  - **Enhances precipitation hardening. A synergistic benefit attributed to Ti addition.**

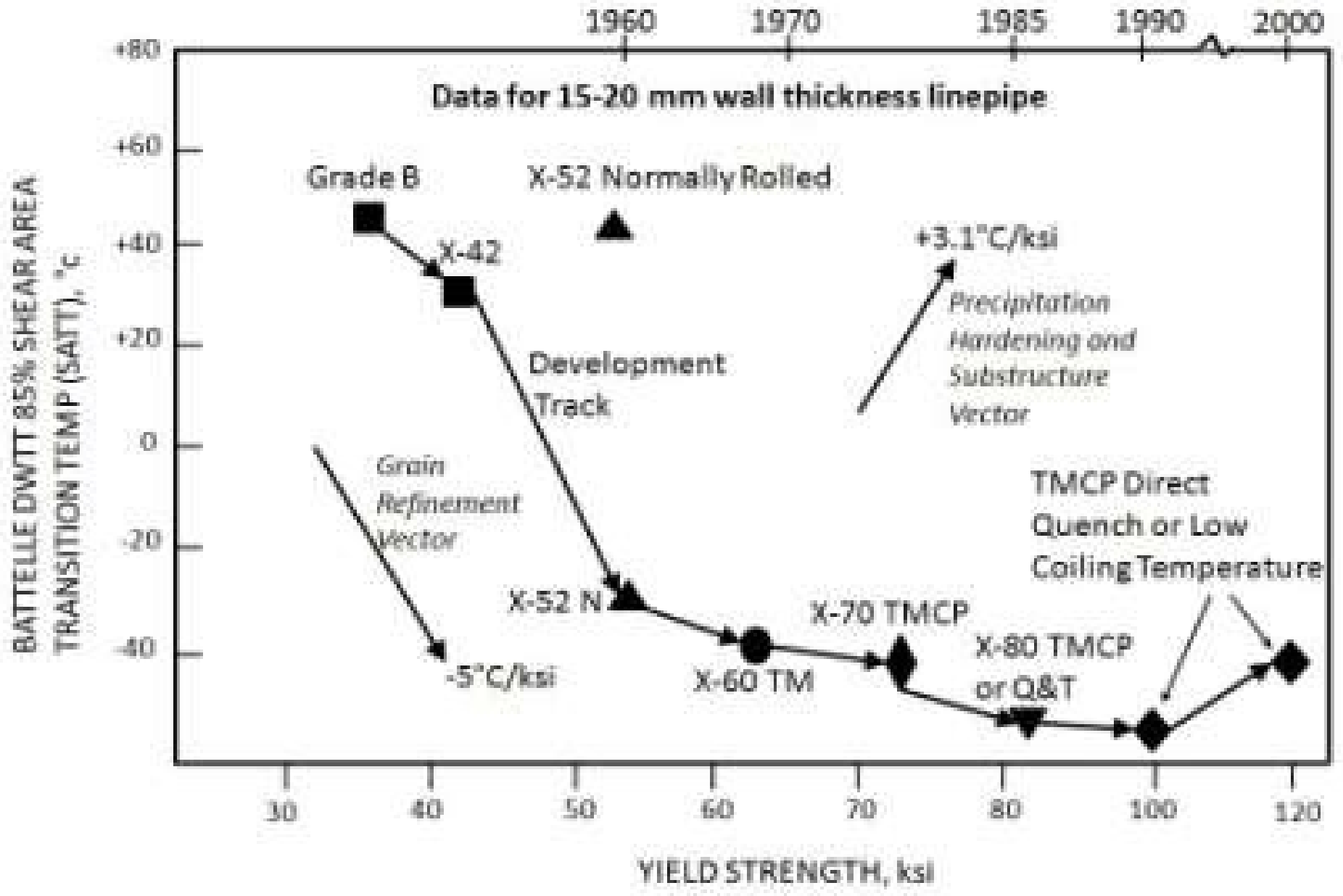
- **In particular, the microalloying of B (< 0.002 wt%) has some particular contributions to API 5L X120, such as:**
  - **Improvement of hardenability by formation of strengthening constituents (e.g. bainite and/or martensite);**
  - **Retards formation of softer ferrite and pearlite constituents during cooling;**
  - **Allows the use of low CE steel compositions to produce high plate strength and enhance grain boundary strength**


Data compiled for 105 steels
produced by 25 manufacturers
Maximum Carbon Content
API-5L 40th Ed.
Maximun Carbon
API-5L 44th Ed.
PSL 2
Sour
Sour
NK-STAF
NSC-UCLB
CARBON (%)
0.28
0.24
0.20
0.16
0.12
0.08
0.04
0
X-52
X-60
X-65
X-70
X-75
X-80
X-100
X-120
YIELD STRENGTH, ksi

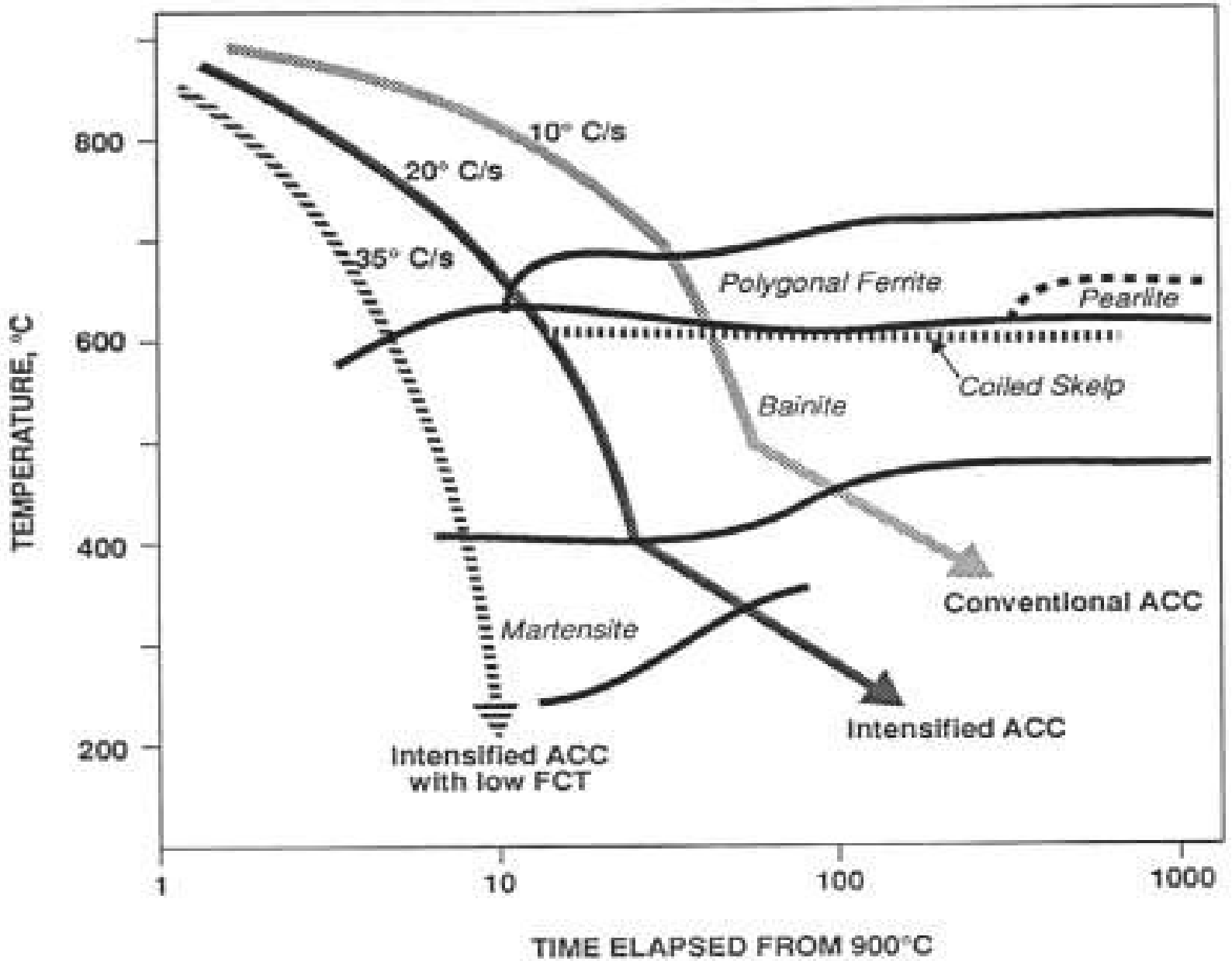
Increasing Strength of Line Pipe Steel With Time

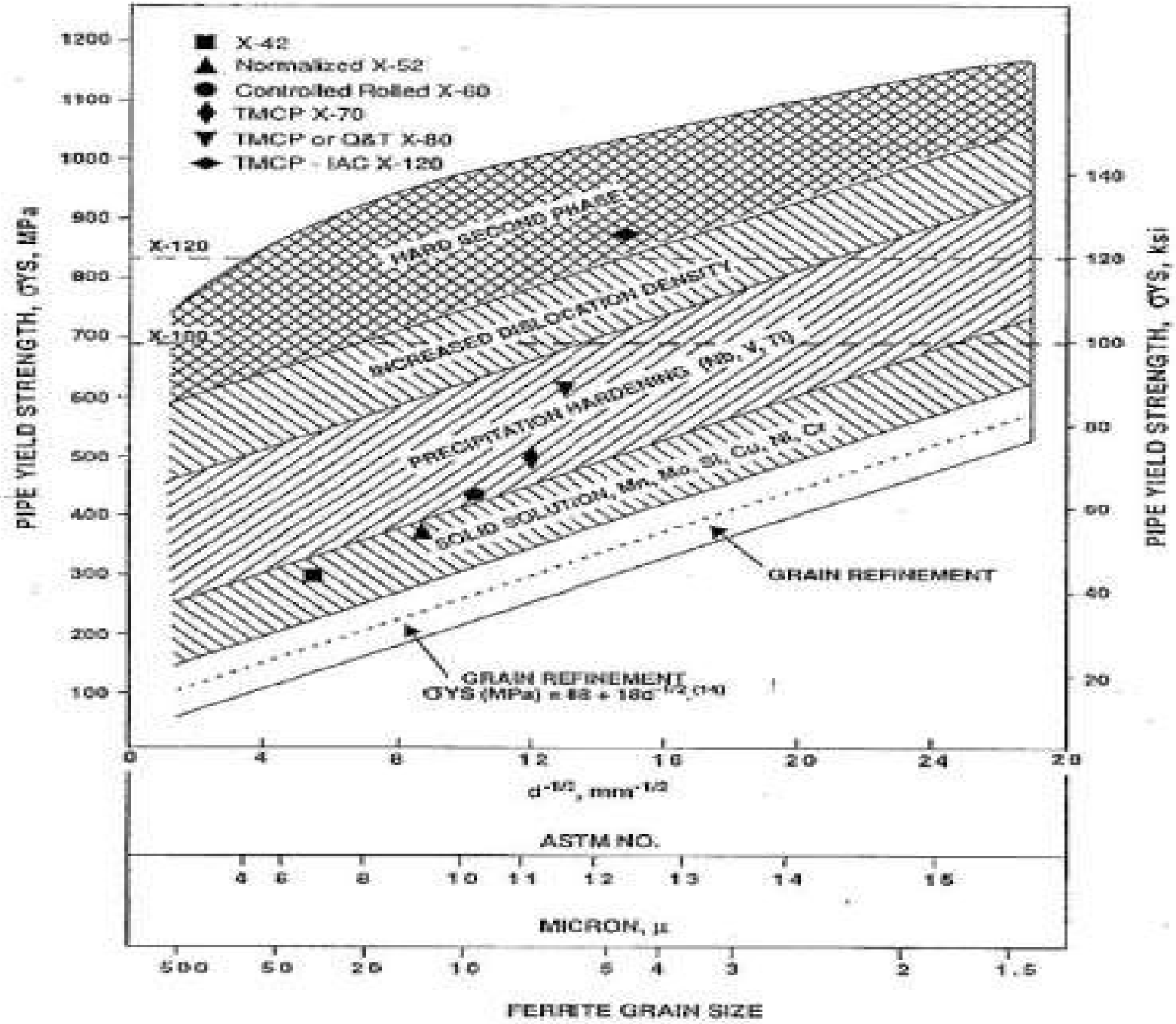


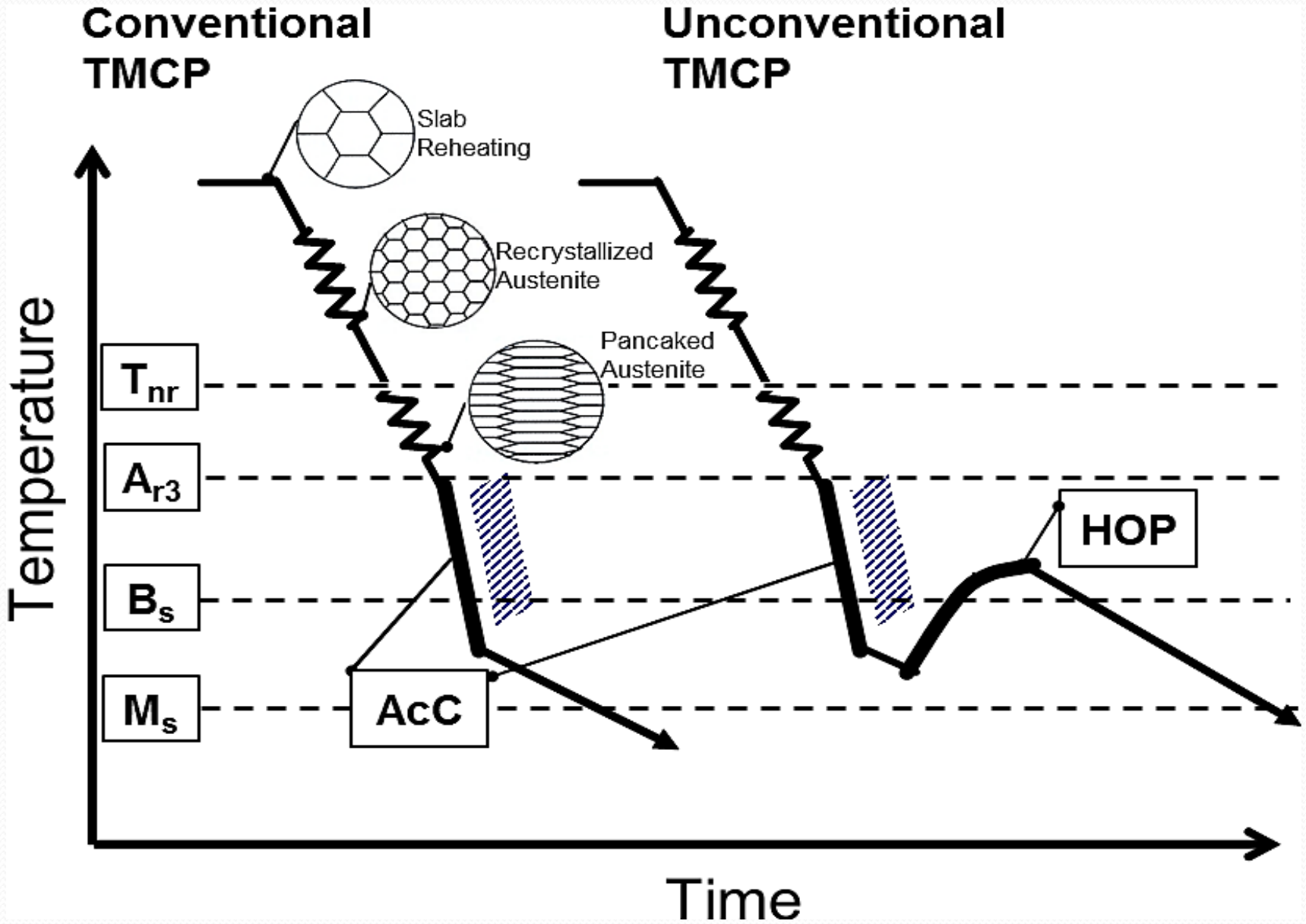
Comparative Toughness Values



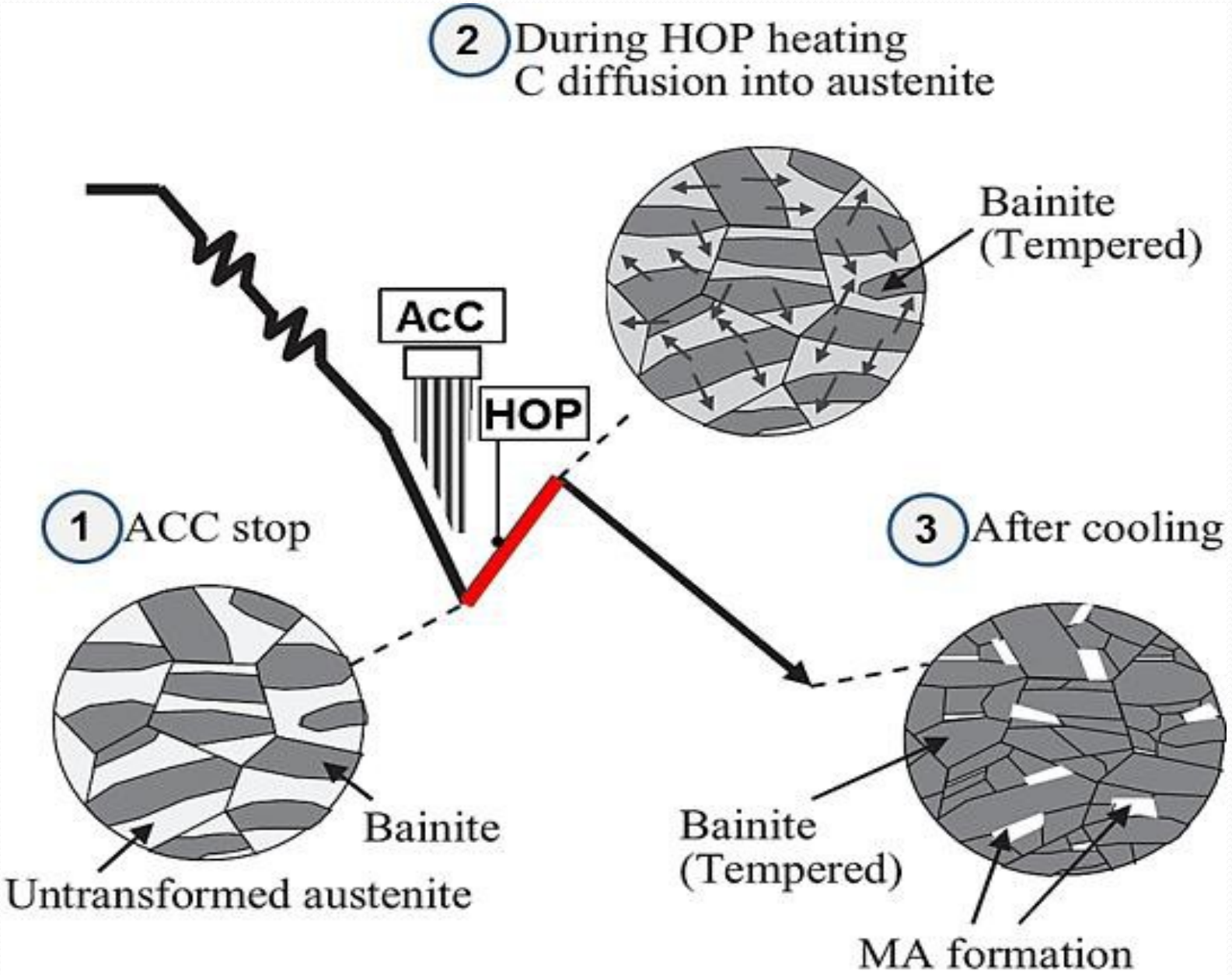
Processing Methods Used




X-42
Normalized X-52
Controlled Rolled X-60
TMCP X-70
TMCP or Q&T X-80
TMCP - IAC X-120
HARD SECOND PHASE
INCREASED DISLOCATION DENSITY
PRECIPITATION HARDENING (Nb, V, Ti)
SOLID SOLUTION (Mn, Mo, Si, Cu, Ni, Cr)
GRAIN REFINEMENT
GRAIN REFINEMENT
σYS (MPa) = 88 + 18d^-1/2 (d)
X-120
X-100
PIPE YIELD STRENGTH, σYS, MPa
PIPE YIELD STRENGTH, σYS, ksi
d^-1/2, mm^-1/2
ASTM NO.
MICRON, μ
FERRITE GRAIN SIZE

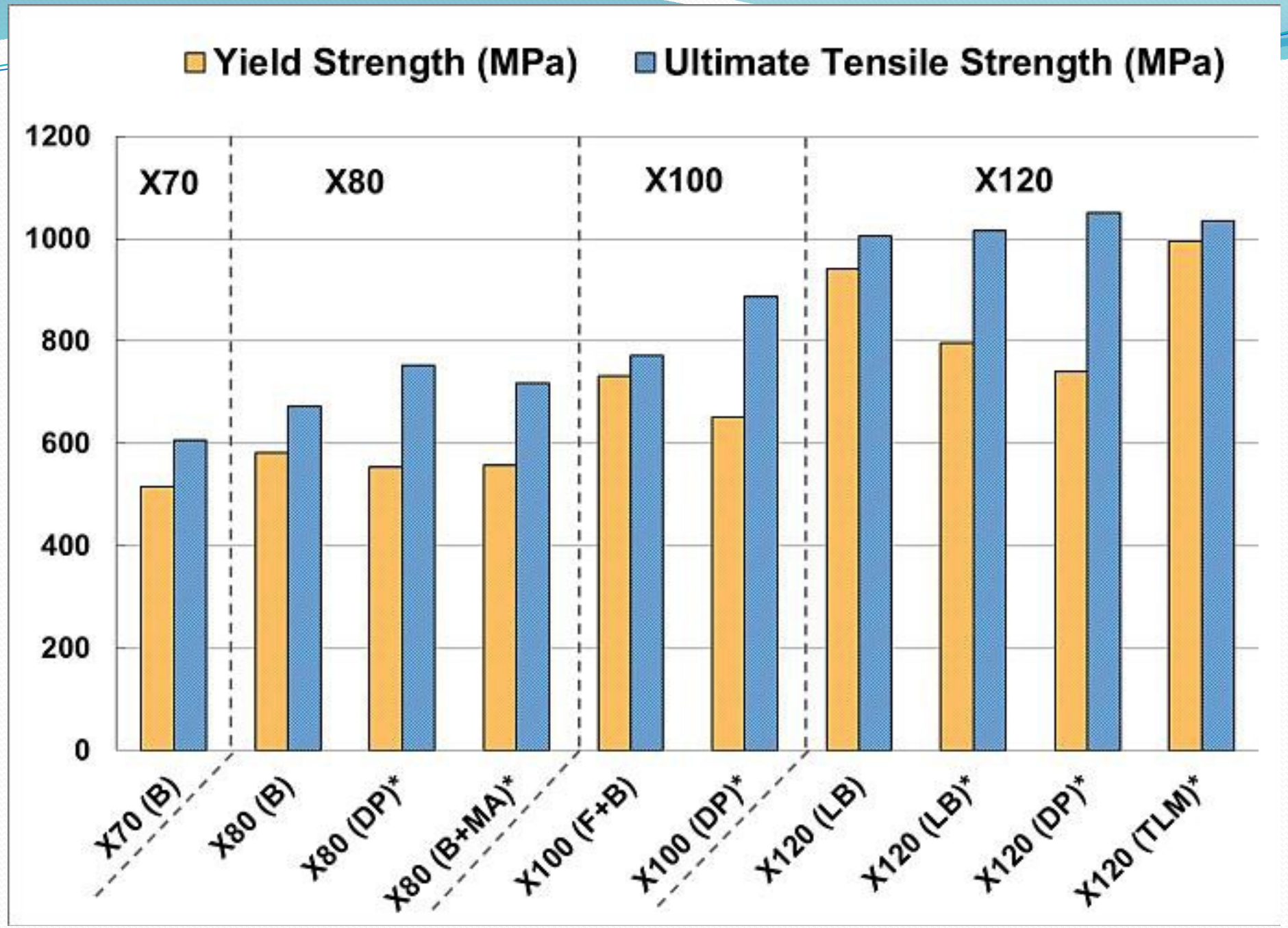

Conventional TMCP
Unconventional TMCP
Slab Reheating
Recrystallized Austenite
Pancaked Austenite
T_{nr}
A_{r3}
B_s
M_s
AcC
HOP
Temperature
Time

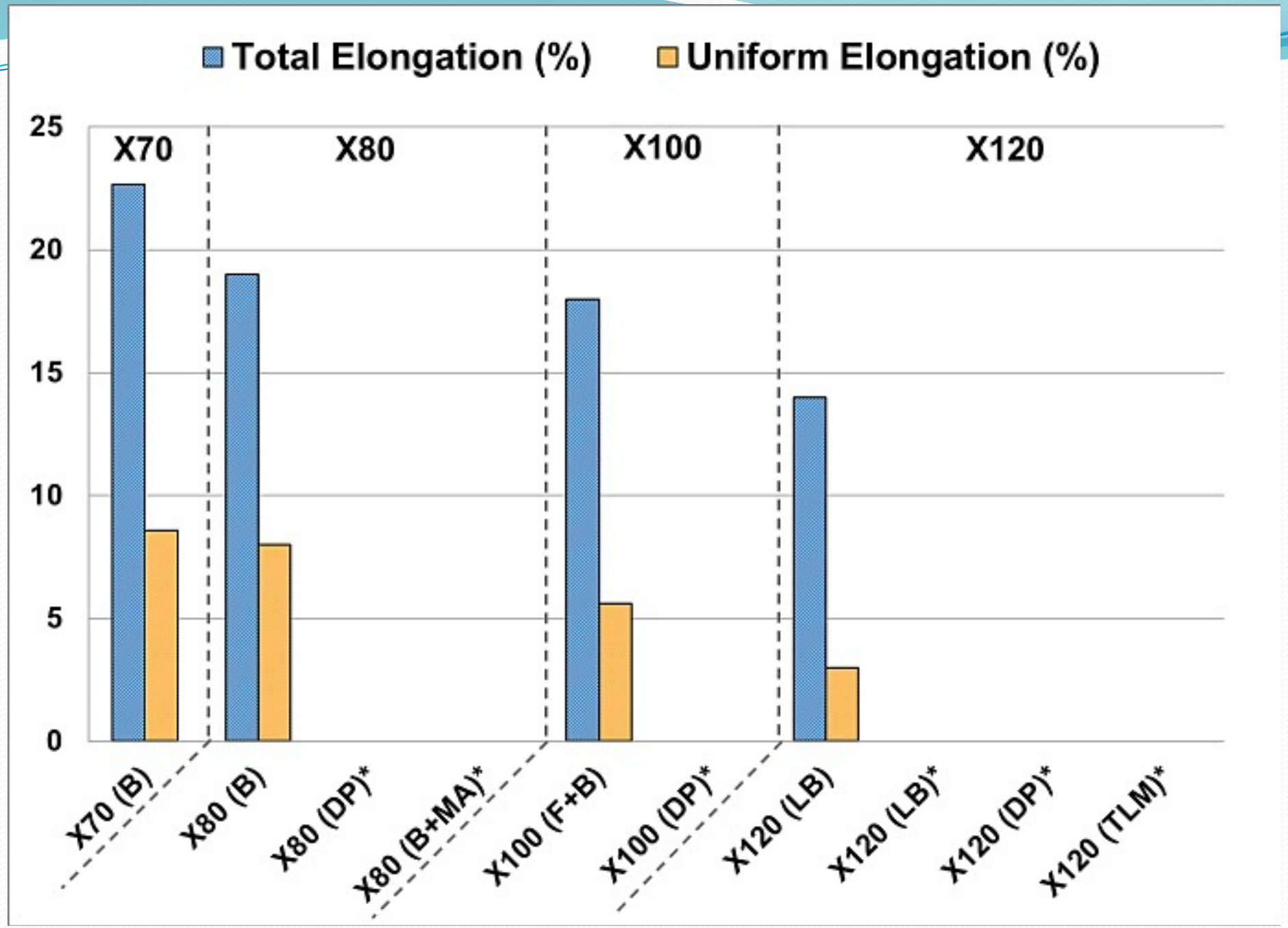
Typical Modern Pipeline Steel Microdtructures

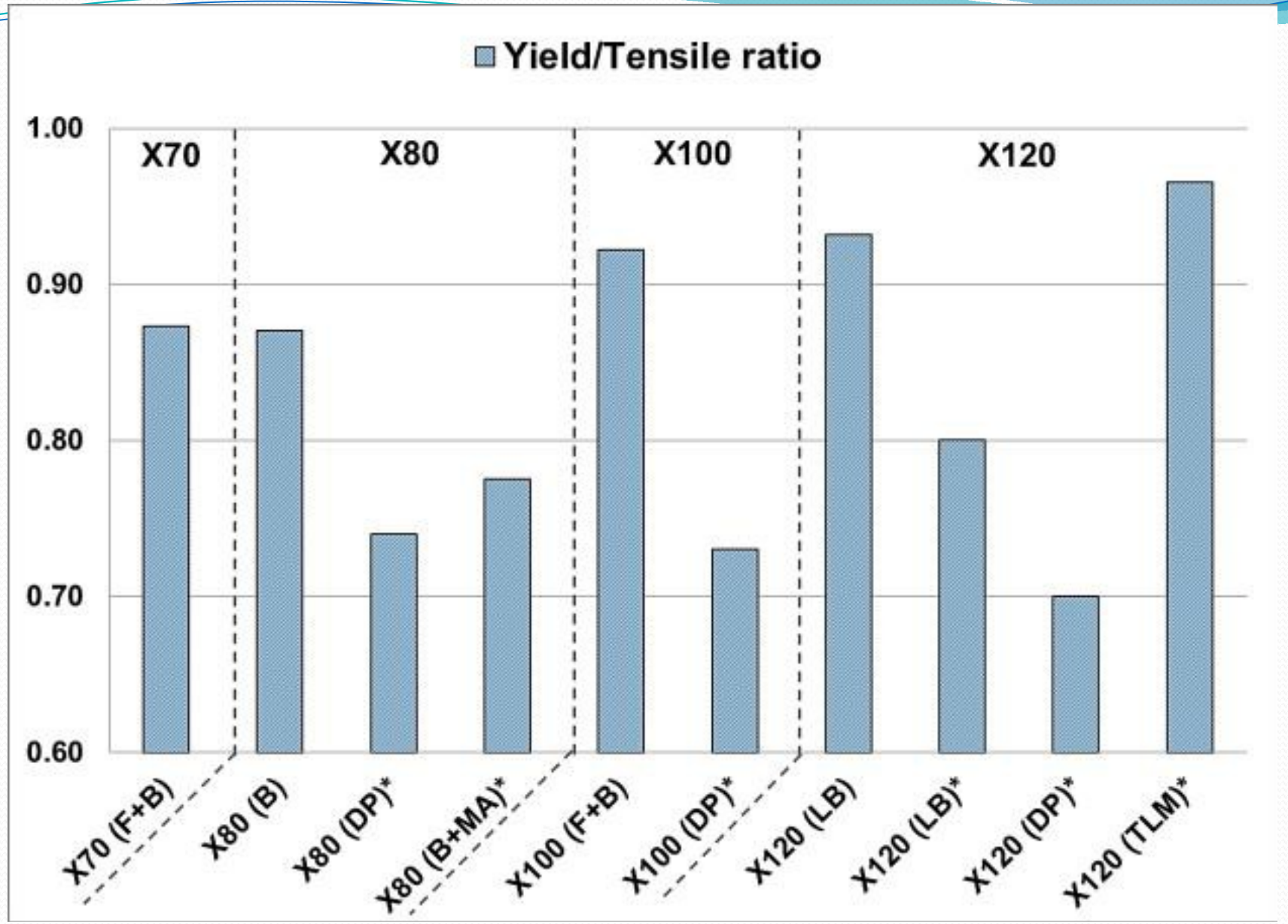


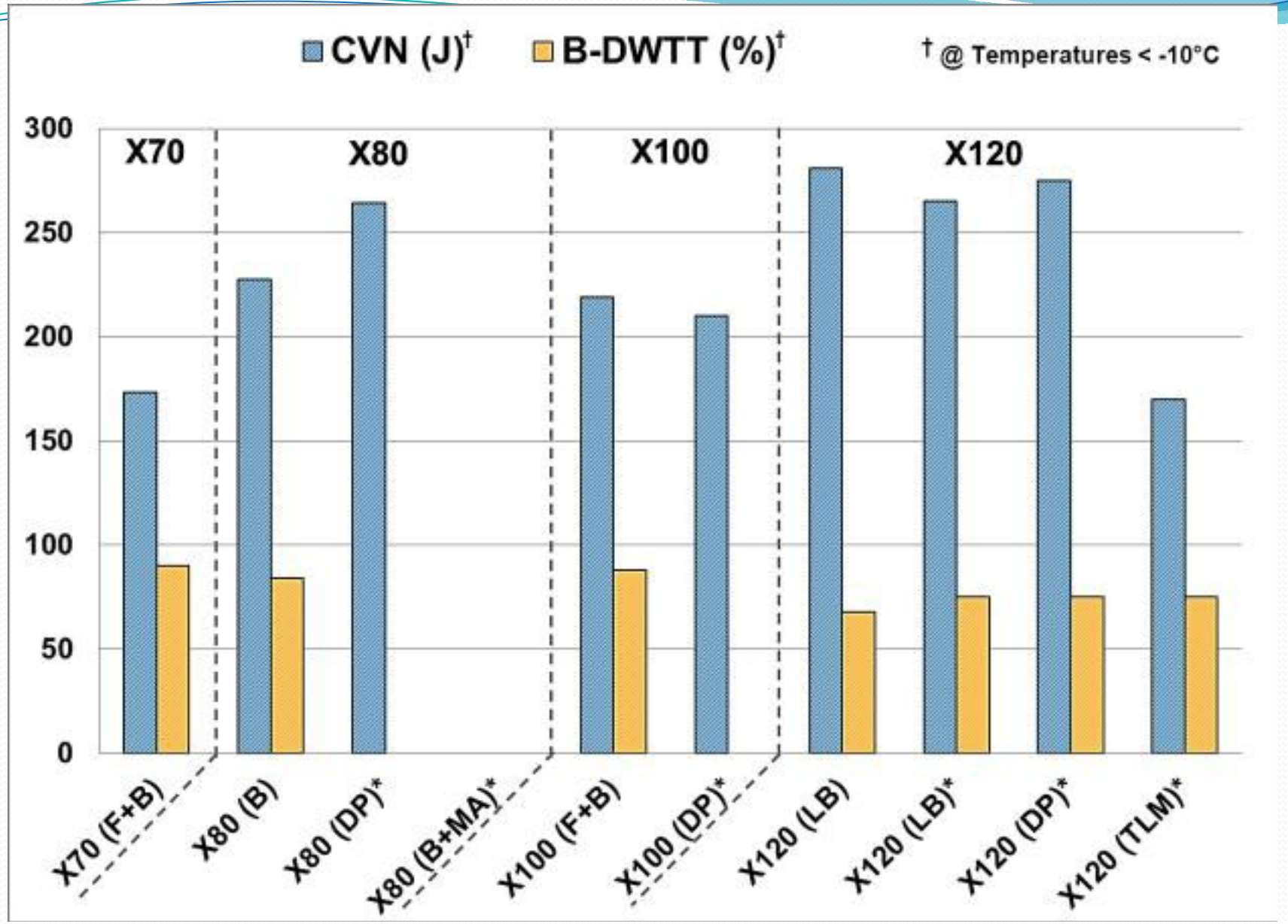
. **Microstructures obtained using different processing conditions.**

API 5L	Processing	Microstructure
X70	TMCP	Polygonal Ferrite (PF) + Pearlite Band (P)
		Bainite (B)
	TMCP + QT	Bainite (B) + Martensite (M) + Ferrite (F)
	TMCP + AcC +QT	Fine-grained Bainite
X80	TMCP + AcC	Lower Bainite (LB)
		Ferrite (F) + Bainite (B) Dual Phase (DP)
		Lower Bainite (B) + Lath Martensite (M)
	TMCP + AcC + HOP	Bainite (B) + Martensite-austenite (MA)
X100	TMCP	Ferrite (F) + Bainite (B)
	TMCP + AcC + HOP	Ferrite (F) + Bainite (B) Dual Phase (DP)


Yield Strength (MPa)
Ultimate Tensile Strength (MPa)
1200
1000
800
600
400
200
0
X70
X80
X100
X120
X70 (B)
X80 (B)
X80 (DP)*
X80 (B+MA)*
X100 (F+B)
X100 (DP)*
X120 (LB)
X120 (LB)*
X120 (DP)*
X120 (TLM)*


Total Elongation (%)
Uniform Elongation (%)
25
20
15
10
5
0
X70
X80
X100
X120
X70 (B)
X80 (B)
X80 (DP)*
X80 (B+MA)*
X100 (F+B)
X100 (DP)*
X120 (LB)
X120 (LB)*
X120 (DP)*
X120 (TLM)*


Yield/Tensile ratio
1.00
0.90
0.80
0.70
0.60
X70
X80
X100
X120
X70 (F+B)
X80 (B)
X80 (DP)*
X80 (B+MA)*
X100 (F+B)
X100 (DP)*
X120 (LB)
X120 (LB)*
X120 (DP)*
X120 (TLM)*


CVN (J)†
B-DWTT (%)†
† @ Temperatures < -10°C
300
250
200
150
100
50
0
X70
X80
X100
X120
X70 (F+B)
X80 (B)
X80 (DP)*
X80 (B+MA)*
X100 (F+B)
X100 (DP)*
X120 (LB)
X120 (LB)*
X120 (DP)*
X120 (TLM)*

Summary

- Pipelines are Vital Structures for economic development of the Nation
- Material specifications are important to economically and successfully build and operate Modern Pipelines.
- It is necessary to carefully formulate material specifications to optimize the cost safety and reliability of modern pipelines.
- A good knowledge of the metallurgical principles and effects of alloying elements, effect of manufacturing processes and performance of materials is of prime importance.
- Designers , operators , owners and engineering professionals need to have a reliable access to these important information for success in their respective operation.
- A professional body such as Indian Pipeline association would be a good source for reliable information needed that can be availed of in cost effective manner indigenously.